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(54) SURFACE TREATMENT BY COPPER FOR PREVENTING FINE CRACK IN FLEXIBLE CIRCUIT

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain a flexible circuit having resistance against both of high cycle-low strain fatigue and low cycle-high strain fatigue.
SOLUTION: In a flexible laminate including a first flexible polymer film, a copper layer having a fine crack preventing layer on at least the single surface thereof and a second flexible polymer film, the fine crack preventing layer is sufficient to prevent a fine crack for at least 50,000,000 bending cycles in the copper layer with a thickness of up to about 18 μm of the flexible laminate and/or for at least 20,000,000 bending cycles in the copper layer with a thickness of up to about 35 μm.

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* NOTICES *

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CLAIMS

[Claim(s)]
[Claim 1] It is the copper layer which has a minute crack prevention layer in one side at least. a flexible layered product -- it is -- following: -- flexible polymer film [of ** a first]; -- this minute crack prevention layer In the copper layer which has the thickness to about 18 micrometers of this flexible layered product Between the bending cycles of at least 50,000,000, And/or, the flexible layered product which includes sufficient copper layer; to prevent a minute crack between the bending cycles of at least 20,000,000 in the copper layer which has the thickness to about 35 micrometers, and the second flexible polymer film.
[Claim 2] The flexible layered product according to claim 1 in which said minute crack prevention layer contains the copper deposited using the acid copper sulfate bath.
[Claim 3] The flexible layered product according to claim 1 in which said minute crack prevention layer contains the black oxide layer which has the thickness of about 0.02 to about 2 micrometers.
[Claim 4] The flexible layered product according to claim 1 in which said minute crack prevention layer contains the brown oxide layer which has the thickness of about 0.01 to about 1 micrometer.
[Claim 5] The flexible layered product according to claim 1 in which this minute crack prevention layer has the thickness of about 25 to about 125A including the chromium layer which said minute crack prevention layer deposited using the chromate solution or the cathode chromium cell.
[Claim 6] The flexible layered product containing the metal layer containing the zinc and chromium which said minute crack prevention layer deposited using the acid electrolyte containing chromium, zinc, and a hydrogen inhibitor and which have the thickness of about 25 to about 125A according to claim 1.
[Claim 7] The flexible layered product according to claim 1 in which said minute crack prevention layer contains the oxide layer formed using the water or the oxygen plasma by which aeration was carried out.
[Claim 8] The flexible layered product containing the zinc metal layer which said minute crack prevention layer deposited using the acid electrolyte containing zinc and a hydrogen inhibitor and which has the thickness of about 2 to about 60A according to claim 1.
[Claim 9] The flexible layered product according to claim 2 in which this minute crack prevention layer has [said minute crack prevention layer] the thickness of about 30 to about 500A, including further at least one nickel tie coat layer and a chromium tie coat layer.
[Claim 10] The flexible layered product according to claim 4 in which said minute crack prevention layer contains further the silane coupling agent layer which has the thickness of about 0.002 to about 0.1 micrometers.
[Claim 11] The flexible layered product according to claim 1 in which said polymer film contains at least one polyimide resin, polyester resin, and a condensation polymer.
[Claim 12] The flexible layered product according to claim 1 in which said copper layer has the thickness to about 70 micrometers.
[Claim 13] The flexible layered product according to claim 1 which contains an adhesion promoter further between said first flexible polymer film and said copper layers.
[Claim 14] The flexible layered product according to claim 1 which contains an adhesion promoter further between said second flexible polymer film and said copper layers.
[Claim 15] The process which attaches to the first flexible polymer film the first field of the process; this copper layer which processes this copper layer in order to prevent the process; minute crack which is the process of production of a flexible layered product and offers the following process:copper layers; a process including the process which attaches to the second field of this copper layer process; and the second flexible polymer film which carry out pattern formation to this copper foil.
[Claim 16] A process including the process contacted to time amount with the process sufficient in order to

offer the minute crack prevention layer which has the thickness of about 0.1 to about 10 micrometers for this copper layer which processes said copper layer in order to prevent a minute crack, and the acid copper sulfate bath containing the copper sulfate of about 0.1 to about 50 g/l according to claim 15.
[Claim 17] The process which is a process according to claim 15, and processes said copper layer in order to prevent a minute crack The process which contacts this copper layer to a hydroxide compound an oxidizer and if needed is included. This oxidizer An ammonium nitrate, an ammonium perchlorate, ammonium persulfate, Nitric-acid tetramethylammonium, nitric-acid tetraethylammonium, sodium chlorite, A sodium hypochlorite, a sodium nitrate, a sodium nitrite, sodium perborate, A fault sodium carbonate, a sodium perchlorate, sodium periodate, sodium persulfate, A potassium nitrate, a potassium nitrite, a perboric acid potassium, a potassium perchlorate, A potassium periodate, potassium persulfate, a nitric-acid rubidium, a perchloric acid rubidium, The process chosen from a magnesium nitrate, magnesium perchlorate, a calcium hypochlorite, a calcium nitrate, perchloric acid calcium, a strontium nitrate, perchloric acid strontium, the water by which aeration was carried out, and the oxygen plasma.
[Claim 18] The process according to claim 15 in which the process which processes said copper layer in order to prevent a minute crack includes the process which contacts this copper layer in the time amount for about 1 to about 100 seconds, and the chromate solution containing the chromate of about 0.1 to about 10 g/l.
[Claim 19] The process according to claim 15 in which the process which processes said copper layer in order to prevent a minute crack includes the process which contacts this copper layer to the cathode chromium cell containing the chromium compound of about 0.1 to about 5 g/l under the time amount for about 2 to about 20 seconds, and the current density of about 10 to about 40 ASF.
[Claim 20] The process according to claim 15 in which the process which processes said copper layer in order to prevent a minute crack includes the process which contacts this copper layer to the cathode chromium cell containing the zinc ion of about 0.1 to about 2 g/l, the chromium ion of about 0.3 to about 5 g/l, and about 5 to about 1000 ppm hydrogen inhibitor under the time amount for about 1 to about 30 seconds, and the current density of about 1 to about 100 ASF.
[Claim 21] The process which is a process according to claim 15, and processes said copper layer in order to prevent a minute crack At least one ammonium nitrate, an ammonium perchlorate, ammonium persulfate, Nitric-acid tetramethylammonium, nitric-acid tetraethylammonium, sodium chlorite, A sodium hypochlorite, a sodium nitrate, a sodium nitrite, sodium perborate, A fault sodium carbonate, a sodium perchlorate, sodium periodate, sodium persulfate, A potassium nitrate, a potassium nitrite, a perboric acid potassium, a potassium perchlorate, A potassium periodate, potassium persulfate, a nitric-acid rubidium, a perchloric acid rubidium, A process including the process which forms an oxide layer on this copper layer using a magnesium nitrate, magnesium perchlorate, a calcium hypochlorite, a calcium nitrate, perchloric acid calcium, a strontium nitrate, perchloric acid strontium, and the water by which aeration was carried out.

[Claim 22] The process according to claim 15 in which the process which processes said copper layer in order to prevent a minute crack includes the process which contacts process; on which a zinc layer is made to deposit by vapor-depositing on :this copper layer below, and this zinc layer to a hexavalent chromium oxide compound.
[Claim 23] The process according to claim 21 which is made to deposit one or more Cu, Fe, V, Ti, aluminum, Si, Pd, Ta, W, Zn, In(s), Sn, Mn, and Co(es) by physical vacuum evaporationo or chemical vacuum evaporationo at least one chromium, nickel, and if needed, and includes further the process which forms the tie coat layer which has the thickness of about 30 to about 500A.
[Claim 24] The process according to claim 21 which includes further the process which makes one or more silane coupling agents deposit on said copper layer which oxidized.
[Claim 25] The flexible circuit containing the first flexible polymer film, a copper layer, and the second flexible polymer film, In the copper layer which has the thickness to about 18 micrometers Between the bending cycles of at least 50,000,000, It is the approach of preventing a minute crack and this flexible circuit accepts the need. Adhesives Between this at least one copper layer and the flexible polymer films of this first, and this copper layer -- this -- the approach of being an approach and including at least the process of :this copper layer which processes one side by the cathode processing in an acid copper sulfate bath, oxidation treatment, chroming, the cathode processing in ****, tie coat processing, and silanizing which includes further between the second flexible polymer film.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] Generally this invention relates to the flexible circuit which has the improved resistance over mechanical fatigue, and this improved production approach of a flexible circuit. Especially this invention relates to processing of the copper layer of the flexible circuit for setting to the copper foil coat of a flexible circuit, and propagation of a minute crack being prevented, minimized and/or delayed.
[0002]
[Description of the Prior Art] A flexible circuit is used in the electronics industry as a basic material for manufacture of an extensive flexible interconnect product (for example, the flexible circuit board and the FREX rigid circuit board). The FREX circuit board and the FREX rigid circuit board are used in a notebook mold computer, a printer, a disk drive, many medical equipments, and consumer products. A flexible circuit is used again for specific advanced application (for example, chip-on flex time and a fine line circuit substrate). In the electronics industry, it has shifted to being thinner and lighter, flexibility, and a more functional product, and the need over a flexible circuit is continuing increasing.
[0003] A flexible circuit consists of one copper layer (copper conductor) inserted between two organic polymer layers conventionally. Pattern formation especially of the copper foil is combined and carried out to a substrate, and a cover layer is applied on copper foil. A flexible circuit is bent while in use, and can be lengthened so that this identifier may suggest. Therefore, in order to maintain electrical characteristics, it is wished for a flexible circuit to have structural advanced integrity. bending of the flexible circuit to which structural maintenance leads electric [poor] -- and -- lengthening -- the resistance over the mechanical fatigue caused is offered.
[0004] The mechanical indication in early stages of fatigue in a flexible circuit is characterized by microscopic crack initiation and microscopic propagation in the front face of a copper foil coat. a microscopic crack -- the inside of the thickness of copper foil -- or width of face is crossed and it may spread. When a flexible circuit is used, a microscopic crack turns into a crack of magnitude which can cross the thickness of copper foil or may finally be led to measurement and which is conspicuous, and the wafer of copper foil separates in the front face of a copper foil coat here. This type to a copper foil coat of damage leads a natural electric defect.
[0005] The crack initiation and the propagation by bending are called "fatigue." ;, i.e., roll fatigue, to which three main types of fatigue are, and bending (flex) fatigue -- and -- bending (fold) -- fatigue. Roll fatigue may mainly originate in two force in the copper foil of a flexible circuit. With reference to drawing 1 , the flexible circuit 10 is moved to the appearance shown by the arrow head 12 forward and backward. This work has copied actuation of a disk drive. An arrow head 14 expresses the tension in the flexible circuit 10 (and [especially] copper foil and here do not show). An arrow head 16 shows the compressive force in the flexible circuit 10 (and [especially] copper foil and here do not show). Then, when the flexible circuit 10 is moved forward and backward along with an arrow head 12, tension and compressive force move forward and backward. The stress which was imposed according to tension and compressive force and which was repeated uniformly draws roll fatigue of the copper foil all over the flexible circuit 10. Bending fatigue is characterized by holding a flexible circuit by two points, and applying normal stress (force normal) to the point of the abbreviation one half during two retaining points in a flexible circuit, then applying another normal stress to a flexible circuit in an opposite (180 degrees) direction. Bending fatigue bends a flexible circuit by 135-degree crookedness first, and, subsequently a flexible circuit is characterized as having 0-2-degree crookedness bending and by lengthening subsequently to 135 degrees and returning. This motion has copied actuation of a printer hinge.

[0006] Generally the three types with main fatigue (roll fatigue, bending fatigue, and bending fatigue) are caused by a high cycle and low distortion fatigue. Fatigue of another type is a low cycle and high distortion fatigue. It is difficult to provide both a high cycle, low distortion fatigue and a low cycle, and high distortion fatigue with the flexible circuit which has resistance.
[0007] With reference to drawing 2 A and 2B, the some spread to the thickness or width of face of copper foil, and the some show the instantiation of a microscopic crack which has not spread. This instantiation is based on the photograph taken by copper foil 1600 times the scale factor of having the thickness of about 18 micrometers.
[0008]
[Problem(s) to be Solved by the Invention] The flexible circuit which has improved electrical characteristics is offered as a result of this invention. The flexible circuit which has improved electrical characteristics shows the improved resistance over mechanical fatigue, therefore shows the improved resistance over damage on a copper foil coat, and, thereby, improves electrical characteristics. The improved resistance over mechanical fatigue can cause [tolerant] enhancement over the minute crack of a copper foil coat.
[0009] Moreover, the flexible circuit which has bending improved in order to introduce a property is also offered as a result of this invention. In this relation, this invention offers the flexible circuit which has the resistance over both a high cycle, low distortion fatigue and a low cycle, and high distortion fatigue.
[0010]
[Means for Solving the Problem] It is the copper layer which has a minute crack prevention layer in one side at least. one operative condition -- like -- setting -- this invention -- flexible polymer film [of ** a first]; -- a minute crack prevention layer In the copper layer which has the thickness to about 18 micrometers of a flexible layered product Between the bending cycles of at least 50,000,000, And/or, it is related with the flexible layered product containing sufficient copper layer; to prevent a minute crack between the bending cycles of at least 20,000,000 in the copper layer which has the thickness to about 35 micrometers, and the second flexible polymer film.
[0011] In another embodiment, this invention relates to the process of production of a flexible layered product. The process which attaches to the first flexible polymer film the first field of the process; copper layer which processes a copper layer in order that this process may prevent the process; minute crack which offers a copper layer; the process which attaches to the second field of a copper layer process; and the second flexible polymer film which carry out pattern formation to a copper layer is included.
[0012] In still more nearly another embodiment this invention The first flexible polymer film, In the copper layer which has the thickness to about 18 micrometers of the flexible circuit containing a copper layer and the second flexible polymer film Between the bending cycles of at least 50,000,000, This flexible circuit accepts the need about the approach of preventing a minute crack. Adhesives It contains further between at least one copper layer and the first flexible polymer film and between a copper layer and the second flexible polymer film. The process of a copper layer which processes one side at least by the cathode processing in an acid copper sulfate bath, oxidation treatment, chroming, the cathode processing in ****, tie coat processing, and silanizing is included.
[0013] It is the copper layer which has a minute crack prevention layer in one side at least. this invention -- following: -- flexible polymer film [of ** a first]; -- this minute crack prevention layer In the copper layer which has the thickness to about 18 micrometers of a flexible layered product Between the bending cycles of at least 50,000,000, And/or, the flexible layered product which includes sufficient copper layer; to prevent a minute crack between the bending cycles of at least 20,000,000 in the copper layer which has the thickness to about 35 micrometers, and the second flexible polymer film is offered.
[0014] In a suitable embodiment, the above-mentioned minute crack prevention layer contains the copper deposited using the acid copper sulfate bath.
[0015] In a still more suitable embodiment, this minute crack prevention layer has [the above-mentioned minute crack prevention layer] the thickness of about 30 to about 500A, including further at least one nickel tie coat layer and a chromium tie coat layer.
[0016] In a suitable embodiment, the above-mentioned minute crack prevention layer contains the black oxide layer which has the thickness of about 0.02 to about 2 micrometers.
[0017] In a suitable embodiment, the above-mentioned minute crack prevention layer contains the brown oxide layer which has the thickness of about 0.01 to about 1 micrometer.
[0018] In a still more suitable embodiment, the above-mentioned minute crack prevention layer contains further the silane coupling agent layer which has the thickness of about 0.002 to about 0.1 micrometers.
[0019] In a suitable embodiment, this minute crack prevention layer has the thickness of about 25 to about

125A including the chromium layer which the above-mentioned minute crack prevention layer deposited using the chromate solution or the cathode chromium cell.
[0020] In a suitable embodiment, the metal layer containing the zinc and chromium which the above-mentioned minute crack prevention layer deposited using the acid electrolyte containing chromium, zinc, and a hydrogen inhibitor and which have the thickness of about 25 to about 125A is included.
[0021] In a suitable embodiment, the above-mentioned minute crack prevention layer contains the oxide layer formed using the water or the oxygen plasma by which aeration was carried out.
[0022] In a suitable embodiment, the zinc metal layer which the above-mentioned minute crack prevention layer deposited using the acid electrolyte containing zinc and a hydrogen inhibitor and which has the thickness of about 2 to about 60A is included.
[0023] In a suitable embodiment, the above-mentioned polymer film contains at least one polyimide resin, polyester resin, and a condensation polymer.
[0024] In a suitable embodiment, the above-mentioned copper layer has the thickness to about 70 micrometers.
[0025] In a suitable embodiment, an adhesion promoter is further included between the flexible polymer film of the above first, and the above-mentioned copper layer.
[0026] In a suitable embodiment, an adhesion promoter is further included between the flexible polymer film of the above second, and the above-mentioned copper layer.
[0027] The process which attaches to the first flexible polymer film the first field of the process; copper layer which processes a copper layer in order that this invention may prevent the process; minute crack which offers the following process:copper layers again; the process of production of a flexible layered product including the process which attaches to the second field of a copper layer process; and the second flexible polymer film which carry out pattern formation to copper foil is offered.
[0028] In a suitable embodiment, the process which processes the above-mentioned copper layer in order to prevent a minute crack includes the process contacted to sufficient time amount and the acid copper sulfate bath containing the copper sulfate of about 0.1 to about 50 g/l, in order to offer the minute crack prevention layer which has the thickness of about 0.1 to about 10 micrometers for a copper layer.
[0029] The process which processes the above-mentioned copper layer in a suitable embodiment in order to prevent a minute crack The process which contacts a copper layer to a hydroxide compound an oxidizer and if needed is included. This oxidizer An ammonium nitrate, an ammonium perchlorate, ammonium persulfate, Nitric-acid tetramethylammonium, nitric-acid tetraethylammonium, sodium chlorite, A sodium hypochlorite, a sodium nitrate, a sodium nitrite, sodium perborate, A fault sodium carbonate, a sodium perchlorate, sodium periodate, sodium persulfate, A potassium nitrate, a potassium nitrite, a perboric acid potassium, a potassium perchlorate, A potassium periodate, potassium persulfate, a nitric-acid rubidium, a perchloric acid rubidium, It is chosen from a magnesium nitrate, magnesium perchlorate, a calcium hypochlorite, a calcium nitrate, perchloric acid calcium, a strontium nitrate, perchloric acid strontium, the water by which aeration was carried out, and the oxygen plasma.
[0030] In a suitable embodiment, the process which processes the above-mentioned copper layer in order to prevent a minute crack includes the process which contacts a copper layer in the time amount for about 1 to about 100 seconds, and the chromate solution containing the chromate of about 0.1 to about 10 g/l.
[0031] In a suitable embodiment, the process which processes the above-mentioned copper layer in order to prevent a minute crack includes the process which contacts a copper layer to the cathode chromium cell containing the chromium compound of about 0.1 to about 5 g/l under the time amount for about 2 to about 20 seconds, and the current density of about 10 to about 40 ASF.
[0032] In a suitable embodiment, the process which processes the above-mentioned copper layer in order to prevent a minute crack includes the process which contacts a copper layer to the cathode chromium cell containing the zinc ion of about 0.1 to about 2 g/l, the chromium ion of about 0.3 to about 5 g/l, and about 5 to about 1000 ppm hydrogen inhibitor under the time amount for about 1 to about 30 seconds, and the current density of about 1 to about 100 ASF.
[0033] The process which processes the above-mentioned copper layer in a suitable embodiment in order to prevent a minute crack At least one ammonium nitrate, an ammonium perchlorate, ammonium persulfate, Nitric-acid tetramethylammonium, nitric-acid tetraethylammonium, sodium chlorite, A sodium hypochlorite, a sodium nitrate, a sodium nitrite, sodium perborate, A fault sodium carbonate, a sodium perchlorate, sodium periodate, sodium persulfate, A potassium nitrate, a potassium nitrite, a perboric acid potassium, a potassium perchlorate, A potassium periodate, potassium persulfate, a nitric-acid rubidium, a perchloric acid rubidium, The process which forms an oxide layer on a copper layer using a magnesium

nitrate, magnesium perchlorate, a calcium hypochlorite, a calcium nitrate, perchloric acid calcium, a strontium nitrate, perchloric acid strontium, and the water by which aeration was carried out is included.
[0034] In a still more suitable embodiment, one or more Cu, Fe, V, Ti, aluminum, Si, Pd, Ta, W, Zn, In(s), Sn, Mn, and Co(es) are made to deposit by physical vacuum evaporationo or chemical vacuum evaporationo at least one chromium, nickel, and if needed, and the process which forms the tie coat layer which has the thickness of about 30 to about 500A is included further.
[0035] In a still more suitable embodiment, the process which makes one or more silane coupling agents deposit on the copper layer by which oxidation was carried out [above-mentioned] is included further.
[0036] In a suitable embodiment, the process which processes the above-mentioned copper layer in order to prevent a minute crack includes the process which contacts process; and the zinc layer on which a zinc layer is made to deposit to a hexavalent chromium oxide compound by vapor-depositing on :copper layer below.
[0037] The flexible circuit where this invention contains the first flexible polymer film, a copper layer, and the second flexible polymer film again, In the copper layer which has the thickness to about 18 micrometers Between the bending cycles of at least 50,000,000, Are the approach of preventing a minute crack and this flexible circuit accepts the need. Adhesives Between at least one copper layer and the first flexible polymer film, And the approach of being an approach and including at least the process of :copper layer which processes one side by the cathode processing in an acid copper sulfate bath, oxidation treatment, chroming, the cathode processing in ****, tie coat processing, and silanizing which includes further is offered between a copper layer and the second flexible polymer film.
[0038]
[Embodiment of the Invention] It sets like 1 operative condition and this invention relates to various processings of the copper layer of the flexible circuit for prevention of the propagation of a minute crack by energy being locally imposed by the repeat of bending and the cycle of ******, minimization, and/or delay. another operative condition -- it sets like and this invention relates to the flexible circuit containing the copper layer processed for the minute crack initiation in a copper layer and prevention of propagation, minimization, and/or delay. Although it does not desire to be restricted by any theory, the various processings for the copper layer of a flexible circuit It is thought that the energy locally imposed on a copper layer is decreased. This energy By at least one of the process which distributes the energy locally imposed over the comparatively big field of a copper layer, and the processes which absorb the energy imposed locally It is typically caused by tension and/or compressive force, and, thereby, the energy imposed on a copper layer is decreased. By reduction of the energy imposed locally, propagation of the minute crack in copper foil is prevented, minimized and/or delayed. The energy imposed locally is the stress or the force applied to the comparatively small part of a substrate, and is characterized by the big force per unit field. The energy imposed locally decreases by at least one of the process (the force per unit field on a copper layer is decreased by it) which re-distributes the energy locally imposed over the comparatively big field of a copper layer, and the processes (the energy which moved to the copper layer by it dissipates) which absorb the energy imposed locally.
[0039] The flexible circuit by this invention contains the first flexible polymer substrate or a film, the copper layer that has a minute crack prevention layer and the second flexible polymer film, or a cover layer. A copper layer contains copper or a copper alloy. A copper alloy contains at least one of copper and aluminum, chromium, zinc, gold, silver, palladium, platinum, nickel, cobalt, titanium, a scandium, and the zirconiums. Adhesives exist if needed between a copper layer and at least one of the first flexible polymer film and the second flexible polymer film.
[0040] One or more cathode processings in an acid copper sulfate bath, oxidation treatment, chroming, zincic acid-ized processing, and the cathode processing in **** are mentioned to copper processing for prevention of propagation of a minute crack, minimization, and/or delay. It sets like 1 operative condition and at least one of tie coat processing and the silanizing is combined with one or more cathode processings in an acid copper sulfate bath, oxidation treatment, chroming, zincic acid-ized processing, and the cathode processing in ****. One side or the both sides of copper foil may be processed according to this invention.
[0041] The flexible circuit containing the copper foil which has a minute crack processing layer by this invention has passed through substantial more many bending cycles as compared with the flexible circuit which does not contain the copper foil which has a minute crack processing layer, before a minute crack takes place (that is, a longer period minute crack is resisted). It set like 1 operative condition, and the flexible circuit containing the copper foil which has a minute crack processing layer by this invention has passed through many [25%] bending cycles as compared with the flexible circuit which does not contain the copper foil which has a minute crack processing layer, before a minute crack takes place. In another

embodiment, the flexible circuit containing the copper foil which has a minute crack processing layer by this invention has passed through many [50%] bending cycles as compared with the flexible circuit which does not contain the copper foil which has a minute crack processing layer, before a minute crack takes place. In still more nearly another embodiment, the flexible circuit containing the copper foil which has a minute crack processing layer by this invention has passed through many [100%] bending cycles as compared with the flexible circuit which does not contain the copper foil which has a minute crack processing layer, before a minute crack takes place. In addition, in still more nearly another embodiment, the flexible circuit containing the copper foil which has a minute crack processing layer by this invention has passed through the bending cycle with much single figure as compared with the flexible circuit which does not contain the copper foil which has a minute crack processing layer, before a minute crack takes place.

[0042] Setting like 1 operative condition, this invention enables prevention of a minute crack between the bending cycles of at least 20,000,000 (roll fatigue) in the copper layer which has the thickness to about 18 micrometers of a flexible circuit. In another embodiment, this invention enables prevention of a minute crack between the bending cycles of at least 50,000,000 (roll fatigue) in the copper layer which has the thickness to about 18 micrometers of a flexible circuit. still more nearly another operative condition -- setting like, this invention enables prevention of a minute crack between the bending cycles of at least 20,000,000 (roll fatigue) in the copper layer which has the thickness to about 35 micrometers of a flexible circuit. in addition, still more nearly another operative condition -- setting like, this invention enables prevention of a minute crack between the bending cycles of at least 30,000,000 (roll fatigue) in the copper layer which has the thickness to about 35 micrometers of a flexible circuit.

[0043] Copper processing includes the cathode processing in an acid copper sulfate bath in which it functions in order to move the local stress on a copper layer to the comparatively big field on a copper layer. Typically, an acid copper sulfate bath is about 5 to about 50 degrees C in temperature, and is about 10 to about 40 degrees C in temperature preferably. An acid copper sulfate bath is a dilution acidity copper sulfate bath preferably. In relation to this, the concentration of the copper sulfate in an acid copper sulfate bath is about 60 g/l from about 0.1 g/l. In another embodiment, the concentration of a copper sulfate is about 30 g/l from about 1 g/l. Setting like 1 operative condition, the minute crack prevention layer obtained in this embodiment has the thickness of about 0.01 to about 30 micrometers. In another embodiment, the minute crack prevention layer obtained in this embodiment has the thickness of about 0.1 to about 10 micrometers.

[0044]

[Example] (Example 1) One is the conventional thing and one offers two flexible layered products which are what is depended on this invention. The first flexible layered product (former) contains the copper layer which has the thickness of about 18 micrometers, one glue line which has the thickness of about 25 micrometers next to one side of copper foil, and two polyimide layers (one side covers the glue line which has the thickness of about 25 micrometers, and another side has the thickness of about 50 micrometers, and pastes it up on a copper layer directly). The copper layer in which the second flexible layered product (based on this invention) has the thickness of about 18 micrometers again, One glue line which has the thickness of about 25 micrometers next to one side of copper foil, and two polyimide layers (one side covers the glue line which has the thickness of about 25 micrometers) and another side has the thickness of about 50 micrometers, and pastes it up on a copper layer directly -- having -- although contained, one side of a copper layer is contacted with the acid copper sulfate bath which contains the copper sulfate of about 50 g/l at sufficient time amount and the temperature of about 30 degrees C, in order to form the minute crack prevention layer which has the thickness of about 1 micrometer.

[0045] The bending cycle same with being shown in drawing 1 is presented with a flexible layered product. At intervals of the cycle of 5,000,000, copper foil is examined under one about 1600 times the scale factor of this, and existence of a minute crack and extent are measured. The first flexible layered product is the cycle of 5,000,000 about some minute cracks, and shows an extensive minute crack (some pierce through copper foil) in the cycle of 10,000,000. The second flexible layered product is the cycle of 20,000,000 about some minute cracks, and shows an extensive minute crack (some pierce through copper foil) in the cycle of 40,000,000.

[0046] The copper processing including oxidation treatment includes use of the oxidizer for oxidizing the front face of the copper layer of a flexible circuit. oxidation treatment -- the comparison of a copper layer -- functioning in order to distribute the energy locally imposed over the large field, and/or in order to absorb the energy imposed locally, energy dissipates in a copper layer by it.

[0047] Setting like 1 operative condition, oxidation treatment includes the process which offers a brown oxide on a copper layer front face. In another embodiment, oxidation treatment includes the process which

offers a black oxide layer on the front face of the copper layer of a flexible circuit. Brown and a black oxide are preferably offered by contacting an oxidizer and the front face of a copper layer under existence of a current. The usual oxidizer contains chlorite, a sulfite, a hypochlorite, and hyposulfite. Typically, a black oxide layer is obtained after more perfect oxidation of copper foil as compared with oxidation of a black oxide. At least one oxidizer concentration and copper foil obtain brown or a black oxide depending on the time amount in contact with an oxidizer. In the embodiment in which it asks for a brown oxide, the concentration of an oxidizer is about 30 g/l from about 15 g/l preferably about 100 g/l from about 10 g/l. In the embodiment in which it asks for a black oxide, the concentration of an oxidizer is about 60 g/l from about 40 g/l preferably about 150 g/l from about 40 g/l. In the embodiment in which it asks for a brown oxide, an oxidizer solution is preferably contacted for about 90 seconds from about 30 seconds from about 10 seconds in copper foil for about 3 minutes. In the embodiment in which it asks for a black oxide, an oxidizer solution is preferably contacted from about 5 minutes from about 3 minutes in copper foil for about 7 minutes for about 10 minutes. In these embodiments, brown oxide layer thickness is about 0.01 micrometers to about 1 micrometer, and black oxide layer thickness is about 0.02 micrometers to about 2 micrometers. In another embodiment, brown oxide layer thickness is about 0.05 micrometers to about 0.2 micrometers, and black oxide layer thickness is about 0.07 micrometers to about 0.5 micrometers.

[0048] (Example 2) One is the conventional thing and one offers two flexible layered products which are what is depended on this invention. The first flexible layered product (former) is the same as that of the first flexible layered product indicated in the example 1. The second flexible layered product (based on this invention) is the same as that of the second flexible layered product of an example 1 for about 6 minutes except making the oxidation solution containing the sodium hypochlorite of about 50 g/l contact, in order to offer a black oxide layer for one side of a copper layer.

[0049] The bending cycle same with being shown in drawing 1 is presented with a flexible layered product. At intervals of the cycle of 5,000,000, copper foil is examined under one about 1600 times the scale factor of this, and existence of a minute crack and extent are measured. The first flexible layered product is the cycle of 5,000,000 about some minute cracks, and shows an extensive minute crack (some pierce through copper foil) in the cycle of 10,000,000. The second flexible layered product is the cycle of 20,000,000 about some minute cracks, and shows an extensive minute crack (some pierce through copper foil) in the cycle of 25,000,000.

[0050] (Example 3) One is the conventional thing and one offers two flexible layered products which are what is depended on this invention. The first flexible layered product (former) is the same as that of the first flexible layered product indicated in the example 1. The second flexible layered product (based on this invention) is the same as that of the second flexible layered product of an example 1 for about 60 seconds except making the oxidation solution containing the sodium hypochlorite of about 20 g/l contact, in order to offer a brown oxide layer for one side of a copper layer.

[0051] The bending cycle same with being shown in drawing 1 is presented with a flexible layered product. At intervals of the cycle of 5,000,000, copper foil is examined under one about 1600 times the scale factor of this, and existence of a minute crack and extent are measured. The first flexible layered product is the cycle of 5,000,000 about some minute cracks, and shows an extensive minute crack (some pierce through copper foil) in the cycle of 10,000,000. The second flexible layered product is the cycle of 25,000,000 about some minute cracks, and shows an extensive minute crack (some pierce through copper foil) in the cycle of 30,000,000.

[0052] In another embodiment, a brown oxide is offered by contacting the solution of copper foil, an oxidizer, and a hydroxide compound. Although copper foil is contacted in this solution through the conventional means of arbitration including a DIP, a spray, wipe, immersion, etc., it is desirable that copper foil is immersed in this solution. It is not necessary to apply a current.

[0053] In this embodiment, about 90 degrees C of temperature of a solution are about 40 degrees C to about 80 degrees C more preferably from about 10 degrees C. It sets like 1 operative condition and copper foil is more preferably placed into an oxidizer solution for about 10 seconds from about 5 seconds for about 20 seconds from about 2 seconds.

[0054] An oxidizer is a compound with the capacity which oxidizes the front face of copper foil. The oxidizer of ammonium, alkali metal, and alkaline earth metal is mentioned to an oxidizer. The vocabulary "ammonium" used in this specification contains both ammonium ion (NH_4^+) and organic ammonium ion (for example, tetramethylammonium, tetraethylammonium, tetrapropylammonium, and tetrabuthyl ammonium ion). A lithium, sodium, a potassium, and a rubidium are mentioned to alkali metal, and sodium and a potassium are desirable. Beryllium, magnesium, calcium, strontium, and barium are mentioned to an

alkaline earth metal, and magnesium and calcium are desirable. Ammonium, alkali metal and alkaline earth metal, chlorite, a hypochlorite, a nitrate, a nitrite, percarbonate, a perboric acid salt, a perchlorate, a periodate, and persulfate are mentioned as the example of an oxidizer.
[0055] In an example, an ammonium nitrate, an ammonium perchlorate, ammonium persulfate, Nitric-acid tetramethylammonium, nitric-acid tetraethylammonium, sodium chlorite, A sodium hypochlorite, a sodium nitrate, a sodium nitrite, sodium perborate, A fault sodium carbonate, a sodium perchlorate, sodium periodate, sodium persulfate, A potassium nitrate, a potassium nitrite, a perboric acid potassium, a fault chlorine potassium, A potassium periodate, potassium persulfate, a nitric-acid rubidium, a perchloric acid rubidium, a magnesium nitrate, magnesium perchlorate, a calcium hypochlorite, a calcium nitrate, perchloric acid calcium, a strontium nitrate, and perchloric acid strontium are mentioned. A sodium hypochlorite, sodium chlorite, and sodium persulfate are mentioned to a desirable oxidizer. About 170 g/l of about 180g /of oxidizers exists [30 / about] in the amount of the range of about 50 to about 160 g/l more preferably l. from about 20 in a solution.
[0056] A hydroxide compound is a compound of the arbitration which has in a solution the capacity to offer the hydroxide ion. The hydroxide of ammonium, alkali metal, and alkaline earth metal is mentioned as the example of a hydroxide compound. Ammonium hydroxide, tetramethylammonium hydroxide, hydroxylation tetraethylammonium, a sodium hydroxide, a potassium hydroxide, a magnesium hydroxide, and a calcium hydroxide are mentioned as the example of a hydroxide compound. Less than about 2 g/l of less than about 5 g/l of less than about 3 g/l of hydroxide compounds exists in the amount of less than about 1.5 g/l preferably in a solution.
[0057] In this embodiment, an oxidizer solution contains a suitable solvent (for example, water, polar organic liquids (for example, alcohol and a glycol), and/or such mixture). A water solution is desirable. Various additives may be included in an oxidizer solution again.
[0058] Setting like 1 operative condition, the ratio in g/l of an oxidizer to a hydroxide compound is about 20:1 at least. In another embodiment, the ratio of an oxidizer to a hydroxide compound is about 30:1 at least. In a desirable embodiment, the ratio of an oxidizer to a hydroxide compound is about 50:1 at least. In the most desirable embodiment, the ratio of an oxidizer to a hydroxide compound is about 60:1 at least. In these embodiments, this ratio is required because of the suitable interaction between an oxidation solution and a metallic foil.
[0059] In this embodiment, an oxide layer has about 50 to about 250A, however the thickness of less than about 250A. In another embodiment, the oxide layer thickness obtained on copper foil is about 75 to about 200A, however less than about 200A. still more nearly another operative condition -- the oxide layer thickness which sets like and is obtained on copper foil is about 100 to about 175A, however less than about 175A.
[0060] The solution containing an oxidizer draws formation of an oxide layer on copper foil. The quality of the oxide layer for dissipating tensile stress and compressive force increases as a result of the comparatively little hydroxide compound which exists in a solution, without processing copper foil in electrolysis.
[0061] (Example 4) One is the conventional thing and one offers two flexible layered products which are what is depended on this invention. The first flexible layered product (former) is the same as the first flexible layered product shown in the example 1. The second flexible layered product (based on this invention) is the same as that of the second flexible layered product of an example 1 except contacting the oxidation solution which contains the sodium hypochlorite of about 90 g/l, and the sodium hydroxide of about 2 g/l at about 50 degrees C for about 7 seconds in one side of a copper layer, in order to offer a brown oxide layer.
[0062] The bending cycle same with being shown in drawing 1 is presented with a flexible layered product. At intervals of the cycle of 5,000,000, copper foil is examined under one about 1600 times the scale factor of this, and existence of a minute crack and extent are measured. The first flexible layered product shows the minute crack (some pierce through copper foil) which is the cycle of 5,000,000 and spread some minute cracks in the cycle of 10,000,000. The second flexible layered product shows the minute crack (some pierce through copper foil) which is the cycle of 25,000,000 and spread some minute cracks in the cycle of 30,000,000.
[0063] In still more nearly another embodiment, by time amount effective for embellishing a front face chemically, and the reinforcement of sufficient level, the plasma can be applied to a copper foil front face, and the resistance over a minute crack is reinforced by it. The plasma used for processing on the front face of a film consists of ionized oxygen which is generated using a nonmetal-ized cathode. The vocabulary "a nonmetal-ized cathode" expresses the cathode which the metal or the metallic oxide has not deposited on

significant level on the front face of a copper layer. The vocabulary "significant level" expresses the level which does not exceed about 0.1 atomic ratios, when it measures by X-ray photoelectron spectroscopy. A nonmetal cathode like a carbon cathode is included in a nonmetal-ized cathode. It sets like 1 operative condition and a specific metal cathode like the cathode which consists of aluminum, Ti, V, and such two or more mixture can be used. A carbon cathode is desirable. A direct current or an alternating current can be used and a direct current is desirable. Plasma gases may be the air which contains the oxygen of about 15 to about 100% of concentration in the one embodiment to oxygen and about 100% or gas-like mixture, and the second one or more gases (for example, N2, Ar, Kr, NH3, N2O, CF4 and CO2, or one or more rare gas). In the one embodiment, a plasma gas is oxygen or air. The pressures in a plasma chamber are about 40 to about 100 mTorr(s) by about 150 mTorr(s) from about 30 mTorr(s), and one embodiment in about 20 to about 200 mTorr(s), and one embodiment typically in the range of about 10 to about 500 mTorr(s), and the one embodiment. Discharge power density is the range of about 0.34 to about 2.41 W/cm2 in about 0.17 to about 6.2 W/cm2, and one embodiment in about 0.1 to about 8 W/cm2, and the one embodiment. The gross energy input to a front face is the range of about 0.4 to about 11.3 J/cm2 in about 0.05 to about 113 J/cm2, and one embodiment in about 0.02 to about 150 J/cm2, and the one embodiment.

[0064] One or more plasma treatment processes can be presented with a copper layer. In the one embodiment, oxidation treatment contacts the oxygen plasma and the front face of the copper layer of a flexible circuit, and includes about 5 micrometers of processes which form the oxide layer which has the thickness of about 0.1 to about 1 micrometer preferably from about 0.01 micrometers.

[0065] (Example 5) One is the conventional thing and one offers two flexible layered products which are what is depended on this invention. The first flexible layered product (former) is the same as the first flexible layered product shown in the example 1. The second flexible layered product (based on this invention) is 150mTorr about one side of a copper layer using the discharge power density of about 4 W/cm2, and is the same as the second flexible layered product of an example 1 except contacting the oxidation plasma containing oxygen.

[0066] The bending cycle same with being shown in drawing 1 is presented with a flexible layered product. At intervals of the cycle of 5,000,000, copper foil is examined under one about 1600 times the scale factor of this, and existence of a minute crack and extent are measured. The first flexible layered product shows the minute crack (some pierce through copper foil) which is the cycle of 5,000,000 and spread some minute cracks in the cycle of 10,000,000. The second flexible layered product shows the minute crack (some pierce through copper foil) which is the cycle of 30,000,000 and spread some minute cracks in the cycle of 40,000,000.

[0067] operative condition another further again -- setting like, oxidation treatment includes moderate oxidation treatment in the inside of the water solution which carried out aeration. A solution contains the water which has sufficient quantity of dissolved oxygen, in order to oxidize the front face of copper foil. In this embodiment, the temperature of the water solution which carried out aeration is about 2 degrees C to about 50 degrees C. In another embodiment, the temperature of the oxidizer water solution which carried out aeration is about 10 degrees C to about 40 degrees C. In still more nearly another embodiment, the temperature of the water solution which carried out aeration is about 15 degrees C to about 30 degrees C. It sets like 1 operative condition and the water solution which carried out aeration of the copper foil is contacted for about 100 seconds from about 1. In another embodiment, the water solution which carried out aeration of the copper foil is contacted for about 50 seconds from about 2. In still more nearly another embodiment, the water solution which carried out aeration of the copper foil is contacted for about 25 seconds from about 5.

[0068] In a desirable embodiment, although water is deionized water, tap water may be used. The water of the water solution which carried out aeration contains about 7 ppm dissolved oxygen at least. In a desirable embodiment, the water of the water solution which carried out aeration contains about 7.5 ppm dissolved oxygen at least. Setting like 1 operative condition, water contains about 8 to about 20 ppm dissolved oxygen. In another embodiment, water contains about 9 to about 15 ppm. Using the gas containing acquisition, the pure oxygen gas, or oxygen of the water which has dissolved oxygen of a high level comparatively, the water containing the dissolved oxygen of specific level may be obtained by carrying out aeration of the water until it reaches desired dissolved oxygen level. The gas containing oxygen contains the mixture of air and oxygen, inactive [one or more], and a nonresponsive gas (for example, hydrogen, nitrogen, helium, neon, an argon, a krypton, and a xenon). Aeration of the water solution which carried out aeration between the processes of this invention is carried out periodically or frequently, and it can maintain the minimum level or the range of the request of dissolved oxygen.

[0069] The oxygen level of the water solution which carried out aeration may be measured periodically or frequently using the well-known means of the arbitration for measuring a dissolved oxygen content. For example, one equipment is Yellow. Springs Instrument Trade name YSI from Company Model 57 Series Dissolved Oxigen It is Meter. The approach of a reagent based on the Winkler method may be used again. Pocket for the set of the dissolved oxygen reagent using a buret titrimetric method, a digital titrimetric method, or a drop count titrimetric method, dissolved oxygen reagent AccuVac (trademark) ampul, and dissolved oxygen Colorimeter (trademark) is Hach. It is more nearly available than Company.
[0070] In this embodiment,;, i.e., the water solution which carried out aeration, in which the water solution which carried out aeration does not contain a metal if needed is characterized, when there is no added metal or metallic compounds. The metal or metallic compounds of a minute amount in tap water and deionized water may be permitted. In another embodiment,;, i.e., the water solution which carried out aeration, in which the water solution which carried out aeration does not contain an organic solvent is characterized, when there is no added organic solvent. In still more nearly another embodiment, a little (less than about 2 % of the weight or less than about 1 % of the weight) organic solvent may exist in tap water or deionized water.
[0071] The oxide layer formed of contact in the water solution by which aeration was carried out to copper foil is very thin. In another embodiment, an oxide layer has the thickness of about 1 to about 25A, however less than about 25A. In another embodiment, the oxide layer thickness obtained on copper foil is about 2 to about 20A, however less than about 20A. still more nearly another operative condition -- the oxide layer thickness which sets like and is obtained on copper foil is about 3 to about 15A, however less than about 15A.
[0072] The water solution containing water and at least 7 ppm dissolved oxygen by which aeration was carried out draws formation of a comparatively thin oxide layer on copper foil. The quality of an oxide layer increases for the result that the dissolved oxygen of the amount of specification exists in a solution, without processing copper foil in electrolysis.
[0073] (Example 6) One is the conventional thing and one offers two flexible layered products which are what is depended on this invention. The first flexible layered product (former) is the same as the first flexible layered product shown in the example 1. In order to offer a thin brown oxide layer, the second flexible layered product (based on this invention) is about 30 degrees C for about 20 seconds about one side of a copper layer, and is the same as the second flexible layered product of an example 1 except contacting the oxidation solution containing about 12 ppm dissolved oxygen.
[0074] The bending cycle same with being shown in drawing 1 is presented with a flexible layered product. At intervals of the cycle of 5,000,000, copper foil is examined under one about 1600 times the scale factor of this, and existence of a minute crack and extent are measured. The first flexible layered product shows the minute crack (some pierce through copper foil) which is the cycle of 5,000,000 and spread some minute cracks in the cycle of 10,000,000. The second flexible layered product shows the minute crack (some pierce through copper foil) which is the cycle of 25,000,000 and spread some minute cracks in the cycle of 30,000,000.
[0075] The copper processing including chroming absorbs the energy which distributed the energy locally imposed over the comparatively big field of a copper layer, and/or was imposed locally, and it functions in order for it to distribute the energy to a copper layer. Setting like 1 operative condition, chroming includes the process which contacts a copper layer and a chromate (CrO3) solution. This may be attained by immersion of the copper layer to the inside of a spray or a chromate solution. A chromate may be guided from many sources of supply containing a potassium chromate and chromic-acid magnesium. Setting like 1 operative condition, the concentration of the chromate in a chromate solution is about 10 g/l from about 0.1g/l. In another embodiment, the concentration of the chromate in a chromate solution is about 5 g/l from about 1 g/l. It sets like 1 operative condition and copper foil is preferably contacted by the chromate solution from about 3 seconds for about 100 seconds from about 1 second for about 10 minutes.
[0076] (Example 7) One is the conventional thing and one offers two flexible layered products which are what is depended on this invention. The first flexible layered product (former) is the same as the first flexible layered product shown in the example 1. The second flexible layered product (based on this invention) is about 25 degrees C in temperature for about 7 seconds about one side of a copper layer, and is the same as the second flexible layered product of an example 1 except contacting the chromate solution containing the chromate of about 2 g/l.
[0077] The bending cycle same with being shown in drawing 1 is presented with a flexible layered product. At intervals of the cycle of 5,000,000, copper foil is examined under one about 1600 times the scale factor

of this, and existence of a minute crack and extent are measured. The first flexible layered product shows the minute crack (some pierce through copper foil) which is the cycle of 5,000,000 and spread some minute cracks in the cycle of 10,000,000. The second flexible layered product shows the minute crack (some pierce through copper foil) which is the cycle of 20,000,000 and spread some minute cracks in the cycle of 30,000,000.

[0078] In another embodiment, chromate treatment includes the cathode processing in a chromate solution. Especially, copper foil is arranged in a chromium content cell. A chromium content cell is a water solution containing the additive which reinforces effectiveness a chromium compound and if needed. A current is applied to this tub, consequently the chromium layer of a cathode deposits in electrolysis on copper foil. A chromium compound is a compound of the arbitration which may make the thin layer of the chromium of a cathode, or chromium deposit on copper foil. Chrome oxide (for example, chromium trioxide), a chromium anhydride, a chromic acid, a hexavalent chromium compound, a dichromate (for example, a potassium dichromate and a sodium dichromate), and a chromate (for example, a chromate potassium, chromate sodium, and chromate magnesium) are mentioned as the example of a chromium compound. About 5 g/l of chromium compounds exists in the amount of about 1 to about 3 g/l preferably from about 0.1 in a chromium content cell.

[0079] The engine-performance enhancement additive of arbitration contains a zinc compound (for example, zinc acetate, a zinc chloride, zinc nitrate, and a zinc sulfate) like a zincky salt.

[0080] It sets like 1 operative condition and about 30 degrees C of temperature of the chromium content cell between electrodeposted processes are about 20 degrees C to about 25 degrees C preferably from about 15 degrees C. pH of a chromium content cell is not important depending on the autonomy of the specific chromium compound of a specific embodiment therefore. The current density which sets like 1 operative condition and is applied to a chromium content cell is about 10 to about 40 ASF. In another embodiment, current density is about 20 to about 30 ASF more preferably about 35 ASF from about 15. Copper foil is placed into sufficient time amount and a chromium content cell, in order [of a up to / a copper foil front face] to enable formation of a uniform cathode chromium layer, although it is comparatively thin. It sets like 1 operative condition and copper foil is more preferably placed [5 / about] for about 10 seconds for about 20 seconds from about 2 into a chromium content cell.

[0081] The thickness of the cathode chromium layer which sets like and is obtained 1 operative condition is about 25 to about 125A. In a desirable embodiment, the thickness of the cathode chromium layer obtained is about 50 to about 100A. Over the whole front face of copper foil, the thickness of a cathode chromium layer is substantially uniform, and follows the profile of the arbitration on the front face of copper foil.

[0082] (Example 8) One is the conventional thing and one offers two flexible layered products which are what is depended on this invention. The first flexible layered product (former) is the same as the first flexible layered product shown in the example 1. It is about 25 degrees C in temperature for about 10 seconds about one side of a copper layer, and the second flexible layered product (based on this invention) is 25ASF, and is the same as the second flexible layered product of an example 1 except contacting the chromium content cell containing the chromium of about 3 g/l.

[0083] The bending cycle same with being shown in drawing 1 is presented with a flexible layered product. At intervals of the cycle of 5,000,000, copper foil is examined under one about 1600 times the scale factor of this, and existence of a minute crack and extent are measured. The first flexible layered product shows the minute crack (some pierce through copper foil) which is the cycle of 5,000,000 and spread some minute cracks in the cycle of 10,000,000. The second flexible layered product shows the minute crack (some pierce through copper foil) which is the cycle of 30,000,000 and spread some minute cracks in the cycle of 40,000,000.

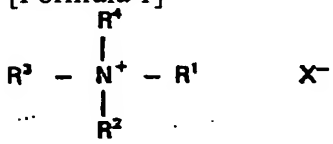
[0084] In still more nearly another embodiment, chroming includes the cathode processing containing zinc and a hydrogen inhibitor like phosphorous acid (phosphorous) in an acid chromate solution. Chroming applies a metal layer to copper foil by contacting copper foil to the electrolytic solution containing zinc ion, chromium ion, and at least one hydrogen inhibitor. The source of supply of the zinc ion for an electrolytic solution may be zinc salt of arbitration. ZnSO4, ZnCO3, ZnCrO4, polyphosphoric acid zinc, sulfamic acid zinc, etc. are mentioned as an example. The source of supply of the chromium ion for an electrolytic solution may be the hexavalent chromium salt or compound of arbitration, and ZnCrO4, CrO3, a chromium trioxide, a chromium anhydride, a hexavalent chromium compound, a dichromate (for example, a potassium dichromate and a sodium dichromate), and a chromate (for example, a potassium chromate, a sodium chromate, and chromic-acid magnesium) are mentioned as an example.

[0085] A hydrogen inhibitor may be an additive of the arbitration of the electrolytic solution of this

embodiment, and checks generating of the hydrogen between application processes. These contain the following ion :P +3, W+6, V+5, As+5, As+3, Pb+2, Pb+4, Hg+1, Hg+2, Cd+2, or quaternary ammonium ion. P+3, W+6, and especially V+5 are desirable. P+3 is very desirable. H3PO3, Na2WO4, Na3VO4, HAsO3, Pb (NO3)2 and Pb (NO3)4, Hg2SO4, HgSO4, CdSO4, etc. are mentioned to the source of supply for these ion.

[0086] Quaternary ammonium ion may be a cation guided from the compound of arbitration, or the following formulas, and is [0087].

[Formula 1]



[0088] Here, in the carbon atom of 1 to about 16, and the one embodiment, R1, R2, R3, and R4 are the hydrocarbon groups of the carbon atom of about 4 independently in the carbon atom of 1 to about 8, and the one embodiment, and X- is an anion (for example, other anions which act as a counter ion of Cl-, OH-, a carbonate, a hydrogencarbonate, a nitrate, or quaternary ammonium). The tetrabuthyl ammonium ion guided from hydroxylation tetrabutylammonium is especially mentioned to desirable quaternary ion.

[0089] Generally the concentration of the zinc ion in an electrolytic solution is the range of about 0.4 to about 0.5 g/l in about 0.3 to about 1 g/l, and another embodiment in about 0.1 to about 2 g/l, and the one embodiment. Generally the concentration of the chromium ion in an electrolytic solution is the range of about 0.5 to about 1.0 g/l in about 0.5 to about 3 g/l, and another embodiment in about 0.3 to about 5 g/l, and the one embodiment. Generally in about 5 ppm to about 1000 ppm, and the one embodiment, the range of the concentration of hydrogen inhibitor ion is about 100 to about 500 ppm. In the one embodiment, the range of the concentration of P+3 ion in an electrolytic solution is about 150 to about 250 ppm in about 100 ppm to about 500 ppm, and one embodiment.

[0090] An electrolytic solution may contain other additives like Na2SO4 by the concentration of the range of about 10 to about 20 g/l by about 1 to about 50 g/l, and the one embodiment. Generally in the about 3 to about 6 and 1 embodiment, the range of pH of an electrolytic solution is about 4 to about five. Generally the current density used is about 30 amps/ft2 in the range of about 25 to about 50 amps/ft2, and another embodiment in the range of about 1 to about 100 amps/ft2, and the one embodiment.

[0091] Generally in about 20 degrees C to about 100 degrees C, and the one embodiment, the range of the temperature of an electrolytic solution is about 25 to about 45 degrees C. Generally the plating time amount adopted is the range for about 5 to about 20 seconds in the one embodiment for about 1 to about 30 seconds. In the one embodiment, the whole processing time of the whole processing time is about 2 to about 8 seconds in another embodiment for about 1 to about 10 seconds.

[0092] In the about 0.2 to about 10 and 1 embodiment, the range of a mole ratio [as opposed to the zinc ion of the chromium ion in an electrolytic solution at one embodiment] is about 1 to about five. In the one embodiment, the range of the mole ratio to the hydrogen inhibitor ion of the zinc ion in an electrolytic solution is about 1 to about two in about 0.4 to about 10 and 1 embodiment.

[0093] Generally, about 0.5 microns of thickness of the cathode layer which is applied to copper foil and which is obtained are set like 1 operative condition from about 0.001, and the range of it is about 0.005 to about 0.01 microns.

[0094] (Example 9) Two flexible layered products are offered, one is the same as before and one follows this invention. The 1st flexible layered product (former) is the same as the 1st flexible layered product indicated by the example 1. The 2nd flexible layered product (this invention is followed) is the same as the 2nd flexible layered product of an example 1, if one side of a copper layer removes contacting the acid cell which is about 25 degrees C in temperature for about 10 seconds, and includes the zinc of about 0.5 g/l, the chromium of about 2 g/l, and about 200 ppm Lynn under 30ASF.

[0095] A bending cycle similar to what is shown in drawing 1 is presented with a flexible layered product. At intervals of 5,000,000 cycles, copper foil is examined by one about 1600 times the dilation ratio of this, and existence of a minute crack and extent are determined. The 1st flexible layered product shows the minute crack of some [5,000,000 cycle], and the minute crack (minding copper foil partly) which spread in 10,000,000 cycles. The 2nd flexible layered product shows the minute crack (minding copper foil partly) which spread in the minute crack of some [35,000,000 cycle], and 45,000,000 cycles.

[0096] Copper processing may include zincic acid-ized processing. Zincic acid-ized processing forms a zinc

oxide, the energy locally imposed in order that this may distribute the energy locally imposed over the comparatively big field of a copper layer is absorbed, and it functions as distributing the energy which operates to a copper layer by it.

[0097] It set like 1 operative condition, and the zinc metal layer was deposited on copper foil, then the zinc-oxide layer was obtained by oxidation. a zinc metal layer -- the thickness of about 2A - about 60A -- having -- another operative condition -- like -- setting -- about 2A - about 50A and still more nearly another operative condition -- like -- setting -- about 5A - about 40A -- still more -- alike -- another operative condition -- it sets like and has the thickness of about 10A - about 35A.

[0098] It sets like 1 operative condition and a zinc metal layer is applied to a copper foil front face using vacuum evaporationo. The vacuum evaporationo technique of well-known arbitration may be used in the field concerned. These include a physical vapor deposition (PVD) and a chemical-vacuum-deposition (CVD) technique. A physical vapor deposition contains heat EPAPORESHON, electron beam deposition, induction and/or resistance deposition, ion plating, sputtering, plasma activity evaporation, reaction EPAPORESHON, and activation reaction evaporation. A physical vapor deposition is quoted as vacuum metallic coating (metallization) and evaporation coating in reference again. or [that a zinc metal evaporates in this case by heating the zinc metal applied to copper foil in a high vacuum in a heat vacuum evaporationo procedure (for example, 10-2 - about ten to 6 torr)] -- or it sublimates and shifts to a copper foil front face. In a sputtering stroke, the ion inactive in energy generated during plasma discharge carries out the impact of the target, and causes emission of a zinc metal by momentum exchange. Compared with the chemical vacuum deposition to which migration of a zinc metal is performed by the chemical reaction guided according to the temperature or the concentration gradient between a substrate and a surrounding gas ambient atmosphere, a physical vapor deposition essentially includes migration of the zinc metal only by the physical means, and formation of the zinc layer on copper foil. An approach useful to vacuum evaporationo of the principle of vacuum evaporationo and various metals is VaporDeposition. The volumes on C.F.Powell, John Wiley&Sons, Inc., New It is indicated by York and 1996 and this is used as reference into this specification.

[0099] Usually chemical vacuum deposition evaporates zinc halide, decomposes or reacts the steam in a foil front face, and is attained by generating a non-volatile zinc metal on the front face of a foil as coating. The chemical reaction of vacuum evaporationo may be performed by heat deposition or a pyrolysis, hydrogen reduction, reduction by metallic fumes, a reaction with copper foil, the chemistry transportation reaction, etc. these procedures -- Vapor Deposition and C.F.Powell ** -- J.Wiley&Sons, Inc., and New York It is indicated by Chapter 9 of 1996 at a detail. This chapter is used as reference into this specification about explanation of a CVD process.

[0100] A zinc metal layer is oxidized by applying the chrome oxide layer of 6 ** to a front face using a well-known electroplating technique. or [converting the chrome oxide of 6 ** into a trivalent chromic-acid ghost between this process] -- or it is returned. the trivalent chrome oxide layer obtained -- about 20A - about 100A in thickness -- having -- one operative condition -- like -- setting -- about 20A - about 60A in thickness, and another operative condition -- it sets like and has about 30A - about 40A in thickness. The raw material of the chrome oxide of 6 ** may be a JIKUROMU acid chloride (Cr2O7=) compound like a chromate (CrO4=) compound like a chromium trioxide (CrO3), a chromyl amide (CrO2(NH2) 2) or a chromyl (CrO2++) compound like chromyl chloride (CrO2Cl2), Na2Cr 2O4, or K2Cr 2O4, Na2Cr 2O7, or K2Cr 2O7. Generally, the concentration of the chrome oxide compound of 6 ** in an electrolyte is in the range of about 1 - about 5 g/l, is set like 1 operative condition, is about 2 - about 4 g/l, and is about 3 g/l in another embodiment. An electrolyte may contain other conventional additives like Na2SO4 by the concentration of within the limits to about 15 g/l, sets them like 1 operative condition, and are 1 to about 15 g/l. pH used for an electrolyte is usually in about 1.5 - about 9 within the limits. Current density is within the limits of about 2 - about 20 amps/ft2, is set like 1 operative condition and is usually within the limits of about 10 - about 20 amps/ft2. The temperature of an electrolyte is within the limits of about 20 - 50 degrees C of abbreviation, is set like 1 operative condition and is usually within the limits of about 35 - 40 degrees C of abbreviation. Usually, the plating time amount used is within the limits of about 2 - about 15 seconds, is set like 1 operative condition, and is about 5 - about 12 seconds.

[0101] A zinc-oxide layer has the thickness of about 3A - about 80A, sets it like 1 operative condition, and it has the thickness of about 5A - about 60A. other operative conditions -- like -- setting -- the thickness of about 10A - about 50A -- having -- and still more nearly another operative condition -- like -- setting -- the thickness of about 15A - about 40A -- having -- and -- still more -- alike -- another operative condition -- it sets like and has the thickness of about 20A - about 35A.

[0102] (Example 10) Two flexible layered products are offered, one is the same as before and one follows this invention. The 1st flexible layered product (former) is the same as the 1st flexible layered product indicated by the example 1. If the 2nd flexible layered product (this invention is followed) removes contacting by vapor-depositing with zinc by Fukashi whose one side of a copper layer is about 60A, it is the same as the 2nd flexible layered product of an example 1. Subsequently, the chrome oxide electrolyte of 6 ** of 3 g/l is contacted under 15ASF during about 10 seconds at about 40 degrees C in the zinc processed by copper foil.
[0103] A bending cycle similar to the layered product shown in drawing 1 is presented with a flexible layered product. At intervals of 5,000,000 cycles, copper foil is examined by one about 1600 times the dilation ratio of this, and existence of a minute crack and extent are determined. The 1st flexible layered product shows the minute crack of some [5,000,000 cycle], and the minute crack (minding copper foil partly) which spread in 10,000,000 cycles. The 2nd flexible layered product shows the minute crack of some [40,000,000 cycle], and the minute crack (minding copper foil partly) which spread in 55,000,000 cycles.
[0104] Copper processing may include deposition of the tie coat (tie coat) combined with one of the above-mentioned copper processings. A tie coat absorbs the energy locally imposed in order to distribute the energy locally imposed over the comparatively big field of a copper layer, and functions as distributing the energy which operates to a copper layer by it. Generally, deposition of a tie coat includes a metaled deposition process.
[0105] Setting like 1 operative condition, tie coat deposition includes deposition of a chromium tie coat. In another embodiment, tie coat processing includes deposition of a nickel tie coat. A chromium tie coat consists of an alloy of chromium or the chromium base. An alloy metal is chosen from Cu, nickel, Fe, V, Ti, aluminum, Si, Pd, Ta, W, Zn, In, Sn, Mn, Co(es), and those two or more mixture. A desirable alloy metal contains Cu, Fe, V, Ti, and nickel. A chromium tie coat layer has the thickness within the limits of about 30A - about 500A, is set like 1 operative condition and has the thickness within the limits of about 50A - about 300A.
[0106] A chromium tie coat layer has a copper seed coat layer adhering to it if needed. A copper seed coat layer has the thickness of about 200A - about 20000A, is set like 1 operative condition and has the thickness of about 1200A - about 5000A.
[0107] A nickel tie coat layer consists of an alloy of nickel or the nickel base. An alloy metal is chosen from Cu, Cr, Fe, V, Ti, aluminum, Si, Pd, Ta, W, Zn, In, Sn, Mn, Co(es), and those two or more mixture. A desirable alloy metal contains Cu, Fe, V, Ti, and Cr. A nickel tie coat layer has the thickness within the limits of about 30A - about 500A, is set like 1 operative condition and has the thickness within the limits of about 50A - about 300A.
[0108] A nickel tie coat layer may have a copper seed coat layer adhering to it if needed. A copper seed coat layer has the thickness of about 200A - about 20000A, is set like 1 operative condition and has the thickness of about 1200A - about 5000A.
[0109] A tie coat may be formed in this contractor using the vacuum evaporationo technique of well-known arbitration, or may be deposited, and such a technique contains a physical vapor deposition (PVD) and chemical vacuum deposition (CVD). In a heat evaporation deposition procedure, by heating the metallicity ingredient for deposition in a high vacuum (for example, basic pressure of less than about 1 mTorr, setting like 1 operative condition basic pressure of about 0.001 mTorr(s)), a metallicity ingredient evaporates, or is sublimated here, and it moves to a substrate. Usually chemical vacuum deposition evaporates a metallicity halogenide, decomposes or reacts the steam in a substrate front face, and is attained by generating a non-volatile metal on the front face of a substrate as coating.
[0110] Sputtering is a useful vacuum evaporationo technique for depositing a tie coat. Including the matter transport phenomenon caused with the ion with which this technique attacks an energy nature atom or a cathode target, the matter which constitutes a cathode target causes the shift to a steamy condition through a moment migration device, and this becomes a different front face as a result. The substrate by which a coat is carried out adjoins a cathode and is arranged. A cathode target consists of matter which forms coating. A negative high electrical potential difference is presented with a cathode, and it is arranged in an inert gas ambient atmosphere in low voltage. Under the effect of a high electrical potential difference, it is accelerated to a cathode label-front face, and the moment of ion shifts to the atom on a cathode label-front face, and atmospheric ions emit an atom from a cathode label-front face here, and cause adhesion in the substrate which these contacted and adjoined. Useful inert gas contains helium, neon, an argon, a krypton, a xenon, etc.
[0111] The metal for deposition is at least one of the alloys of the alloy of Cr and Cr base, nickel, and nickel

base. A useful alloy metal includes Cu, Cr, Fe, V, Ti, aluminum, nickel, Si, Pd, Ta, W, Z, In, Sn, Mn, Co (es), and those combination of two or more pieces. A desirable alloy metal contains Cu, Fe, Cr, nickel, and V. Especially useful commercial nickel alloy Monel (about 67%nickel, 30%Cu), Inconel (about 76%nickel, 16%Cr, 8%Fe), nickel "A" (about 99.4%nickel+Co), nickel "D" (about 95%nickel, 4.5%Mn) and Duranickel (about 94%nickel --) 4.5%aluminum, cast nickel (about 97%nickel, 1.5%Si), "K" Monel (about 66%nickel, 29%Cu, 3%aluminum) and Monel (cast) (about 63%nickel --) 30%Cu, 1.5%Si, and "H" Monel (cast) (about 63%nickel --) 30%Cu, 3%Si, and "S" Monel (cast) (about 63%nickel --) 30%Cu, 4%Si, and Inconel (cast) (about 72%nickel --) 16%Cr, 8%Fe, 2%Si, and nickel-o-flannel (about 42%nickel --) 30%Fe, 22%Cr, 3%Mo, 2%Cu, 1%Ti, and the Hastelloy (Hastelloy) alloy B (about 62%nickel --) 28%Mo, 5%Fe, and the Hastelloy alloy C (about 54%nickel and 17%Mo --) 15%Cr, 5%Fe, and 4%W Hastelloy alloy D (about 85%nickel --) 10%Si, 3%Cu, and the Hastelloy alloy F (it Cr(s) about 47%nickel -- 22%) 7%Mo, 17%Fe, and the Hastelloy alloy N (about 70%nickel and 17%Mo --) 7%Cr, 5%Fe, and the Hastelloy alloy W (about 62%nickel and 24.5%Mo --) 5%Cr, 5.5%Fe, and the Hastelloy alloy X (it Cr(s) about 47%nickel -- 22%) 9%Mo, 18%Fe, and Illium B (it Cr(s) about 50%nickel -- 28%) 8.5%Mo, 5.5%Cu, and Illium G (it Cr(s) about 56%nickel -- 22.5%) 6.5%Mo, 6.5%Cu, and Illium R (it Cr(s) about 68%nickel -- 21%) 5%Mo, 3%Cu, and Illium 98 (it Cr(s) about 55%nickel -- 28%) Mo, 5.5%Cu, (about 80%nickel, 20%Cr), (about 60%nickel, 24%Fe, 16%Cr), (about 35%nickel, 45%Fe, 20%Cr), etc. are included 8.5% (about 45%nickel, 55%Cu). A pressure is within the limits of about 1.5 - about 15 mTorr(s), is set like 1 operative condition and is within the limits of about 2.5 - about 10 mTorr(s).

[0112] Since a copper seed layer is deposited if needed, a pressure is within the limits of about 1.5 - about 15 mTorr(s), is set like 1 operative condition and is within the limits of about 2.5 - about 10 mTorr(s). It is about 200A - about 20000A, and the thickness of the deposited copper seed coat layer is set like 1 operative condition, and is about 1200A - about 5000A.

[0113] (Example 11) Two flexible layered products are given, one is the same as before and one follows this invention. The 1st flexible layered product (former) is the same as the 1st flexible layered product indicated by the example 1. If the 2nd flexible layered product (this invention is followed) removes depositing on one side of a copper layer the copper seed layer which has the thickness of about 2000A through PVD under the pressure of 8mTorr(s) in addition to acid copper-sulfate processing, it is the same as the 2nd flexible layered product of an example 1. Next, the chromium layer which has the thickness of about 250A is deposited through PVD over a copper seed layer under the pressure of 8mTorr.

[0114] A bending cycle similar to what was shown in drawing 1 is presented with a flexible layered product. At intervals of 5,000,000 cycles, copper foil is examined by one about 1600 times the dilation ratio of this, and existence of a minute crack and extent are determined. The 1st flexible layered product shows the minute crack of some [5,000,000 cycle], and the minute crack (minding copper foil partly) which spread in 10,000,000 cycles. The 2nd flexible layered product shows the minute crack of some [45,000,000 cycle], and the minute crack (minding copper foil partly) which spread in 55,000,000 cycles.

[0115] (Example 12) Two flexible layered products are offered, one is the same as before and one follows this invention. The 1st flexible layered product (former) is the same as the 1st flexible layered product indicated by the example 1. If the 2nd flexible layered product (this invention is followed) removes depositing on one side of a copper layer the copper seed layer which has the thickness of about 2000A through PVD under the pressure of 8mTorr(s) in addition to acid copper-sulfate processing, it is the same as the 2nd flexible layered product of an example 1. Next, the Hastelloy alloy D as a source of a metal is used for the nickel alloy layer which has the thickness of about 250A, and it deposits it through PVD over a copper seed layer under the pressure of 8mTorr.

[0116] A bending cycle similar to what was shown in drawing 1 is presented with a flexible layered product. At intervals of 5,000,000 cycles, copper foil is examined by one about 1600 times the dilation ratio of this, and existence of a minute crack and extent are determined. The 1st flexible layered product shows the minute crack of some [5,000,000 cycle], and the minute crack (minding copper foil partly) which spread in 10,000,000 cycles. The 2nd flexible layered product shows the minute crack of some [50,000,000 cycle], and the minute crack (minding copper foil partly) which spread in 60,000,000 cycles.

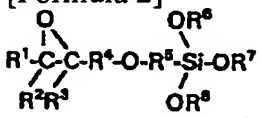
[0117] The copper processing including silanizing includes deposition of at least one silane compound on the copper layer of a flexible circuit by making tie coat processing into an exception combining one of the above-mentioned copper processings. The copper processing including silanizing absorbs the energy imposed locally, and it functions as distributing the energy which can operate to a copper layer by it.

[0118] Setting like 1 operative condition, silanizing includes deposition of one silane compound on another unsettled copper layer. Silanizing is attained by applying one of the silane coupling agents shown below to

copper foil. It is here. :R4-nSiXn to which a silane coupling agent may be expressed by the following formulas -- R is the hydrocarbon group permuted in functional group, and the functional-group-substituent of the hydrocarbon group permuted like the above-mentioned functional group They are amino, a hydroxy ** halo, mercapto, alkoxy ** acyl, or epoxy.;X It is alkoxy one, hydroxyl, or a hydrolysis nature machine like a halogen (for example, chlorine) (for example, methoxy, ETOKISHI, etc.), and;n is 1, 2, or 3, and n is 3 preferably. The silane coupling agent expressed by the above-mentioned formula contains a halo silane, amino alkoxysilane, an aminophenyl silane, phenylsilane, a heterocycle type silane, N-heterocycle type silane, an acrylic silane, mercapto silanes, and those two or more mixture.

[0119] A silane coupling agent is : [0120] which may be expressed by the following formulas.

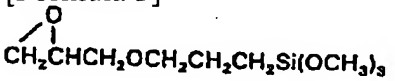
[Formula 2]



[0121] R1, R2, and R3 are hydrogen or a hydrocarbon group independently,;R4 and R5 are alkylene or an alkylidene radical independently here, and;R6, and R7 and R8 are hydrocarbon groups independently. A hydrocarbon group has the carbon atom of 1 - ten abbreviation preferably, still more preferably, has the carbon atom of 1 - six abbreviation, and has the carbon atom of 1 - four abbreviation still more preferably. These hydrocarbon groups are alkyls preferably. an alkylene group or the alkylidene radicals R4 and R5 -- desirable -- 1- about ten carbon atoms -- having -- further -- desirable -- 1- about six carbon atoms -- having -- further -- desirable -- 1- it has about four carbon atoms and has 1-2 carbon atoms still more preferably. An alkylene group and an alkylidene radical may be methylene, ethylene, a propylene, etc. Setting like 1 operative condition, a silane coupling agent is a compound expressed with the following formulas.

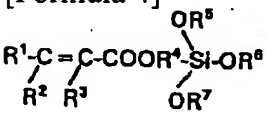
[0122]

[Formula 3]



[0123] A silane coupling agent is : [0124] which may be expressed with the following formulas.

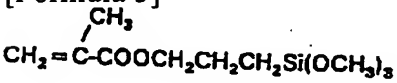
[Formula 4]



[0125] R1, R2, and R3 are hydrogen or a hydrocarbon group independently,;R4 are an alkylene group or an alkylidene radical here, and;R5, and R6 and R7 are hydrocarbon groups independently. A hydrocarbon group has the carbon atom of 1 - ten abbreviation preferably, still more preferably, has the carbon atom of 1 - six abbreviation, and has the carbon atom of 1 - four abbreviation still more preferably. These hydrocarbon groups are alkyls preferably (for example, methyl, ethyl, propyl, etc.). An alkylene group or an alkylidene radical has the carbon atom of 1 - ten abbreviation preferably, still more preferably, has the carbon atom of 1 - six abbreviation, and has the carbon atom of 1 - four abbreviation still more preferably. An alkylene group contains methylene, ethylene, a propylene, etc. Setting like 1 operative condition, a silane coupling agent is a compound expressed with the following formulas.

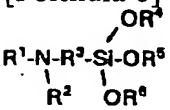
[0126]

[Formula 5]

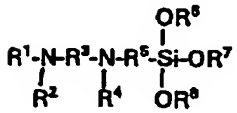


[0127] A silane coupling agent is : [0128] which may be expressed with the following formulas.

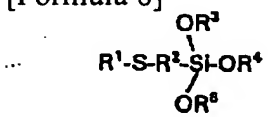
[Formula 6]



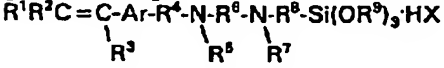
[0129] R1 and R2 are hydrogen or a hydrocarbon group independently,;R3 are an alkylene group or an alkylidene radical here, and;R4, and R5 and R6 are hydrocarbon groups independently. A hydrocarbon group has the carbon atom of 1 - ten abbreviation preferably, still more preferably, has the carbon atom of 1 - six abbreviation, and has the carbon atom of 1 - four abbreviation still more preferably. These hydrocarbon groups are alkyls preferably (for example, methyl, ethyl, propyl, etc.). An alkylene group or an alkylidene radical has the carbon atom of 1 - ten abbreviation preferably, still more preferably, has the carbon atom of 1 - six abbreviation, and has the carbon atom of 1 - four abbreviation still more preferably. An alkylene group contains methylene, ethylene, a propylene, etc. Setting like 1 operative condition, this compound is a compound expressed with the following formulas.
[0130] H2NCH2CH2CH2Si(OC2H5) 3 silane coupling agent is : [0131] which may be expressed with the following formulas.
[Formula 7]



[0132] R1, R2, and R4 are hydrogen or a hydrocarbon group independently,;R3 and R5 are an alkylene group or an alkylidene radical independently here, and;, and R6, R7 and R8 are hydrocarbon groups independently. A hydrocarbon group has the carbon atom of 1 - ten abbreviation preferably, still more preferably, has the carbon atom of 1 - six abbreviation, and has the carbon atom of 1 - four abbreviation still more preferably. These hydrocarbon groups are alkyls preferably (for example, methyl, ethyl, propyl, etc.). An alkylene group or an alkylidene radical has the carbon atom of 1 - ten abbreviation preferably, still more preferably, has the carbon atom of 1 - six abbreviation, and has the carbon atom of 1 - four abbreviation still more preferably. An alkylene group contains methylene, ethylene, a propylene, etc. Setting like 1 operative condition, this compound is a compound expressed with the following formulas.
[0133]
H2NCH2CH2NHCH2CH2CH2Si(OCH3) 3 silane coupling agent may be expressed with the following formulas.
[0134]
[Formula 8]



[0135] R1 is hydrogen or a hydrocarbon group,;R2 are an alkylene group or an alkylidene radical here, and;R3, and R4 and R5 are hydrocarbon groups independently. A hydrocarbon group has the carbon atom of 1 - ten abbreviation preferably, still more preferably, has the carbon atom of 1 - six abbreviation, and has the carbon atom of 1 - four abbreviation still more preferably. These hydrocarbon groups are alkyls preferably (for example, methyl, ethyl, propyl, etc.). An alkylene group or an alkylidene radical has the carbon atom of 1 - ten abbreviation preferably, still more preferably, has the carbon atom of 1 - six abbreviation, and has the carbon atom of 1 - four abbreviation still more preferably. These radicals are alkylenes preferably (for example, methylene, ethylene, a propylene, etc.). It is : [0136] to which it sets like 1 operative condition and the :HSCH2CH2CH2Si(OCH3) 3 silane coupling agent to which this compound is expressed with the following formulas may be expressed with the following formulas.
[Formula 9]



[0137] here -- R1, R2, R3, R5, and R7 -- becoming independent -- hydrogen or a hydrocarbon group -- it is --;R4, and R6 and R8 -- becoming independent -- an alkylene group or an alkylidene radical -- it is --; -- each R9 is a hydrocarbon group independently,;Ar is an aromatic series radical, and; and X are halogens. A hydrocarbon group has the carbon atom of 1 - ten abbreviation preferably, still more preferably, has the carbon atom of 1 - six abbreviation, and has the carbon atom of 1 - four abbreviation still more preferably. These hydrocarbon groups are alkyls preferably (for example, methyl, ethyl, propyl, etc.). An alkylene group or an alkylidene radical has the carbon atom of 1 - ten abbreviation preferably, still more preferably, has the carbon atom of 1 - six abbreviation, and has the carbon atom of 1 - four abbreviation still more

preferably. These radicals are alkylenes preferably (for example, methylene, ethylene, a propylene, etc.). The aromatic series radical Ar is a single nucleus (for example, phenylene), and may be polykaryotic (for example, naphthylene) which has profit or a single nucleus, especially its phenylene is desirable. A halogen and X are chlorine preferably [it is desirable and] to chlorine or a bromine, and a pan. Setting like 1 operative condition, this compound is a compound expressed with the following formulas.

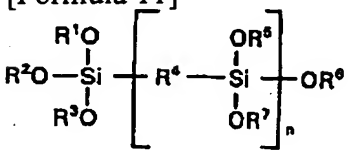
[0138]

[Formula 10]

$CH_2=CHC_6H_4CH_2NHCH_2CH_2NH(CH_2)_3Si(OCH_3)_3\cdot HCl$

[0139] A silane coupling agent is : [0140] which may be expressed with the following formulas.

[Formula 11]



[0141] R1, R2, R3, R5, R6, and R7 are hydrocarbon groups independently,;R4 are an alkylene group or an alkylidene radical here, and; and n are 0 or 1. A hydrocarbon group has the carbon atom of 1 - ten abbreviation preferably, still more preferably, has the carbon atom of 1 - six abbreviation, and has the carbon atom of 1 - four abbreviation still more preferably. These hydrocarbon groups are alkyls preferably (for example, methyl, ethyl, propyl, etc.). An alkylene group or an alkylidene radical has the carbon atom of 1 - ten abbreviation preferably, still more preferably, has the carbon atom of 1 - six abbreviation, and contains the carbon atom of 1 - four abbreviation still more preferably. This radical is alkylene preferably (for example, methylene, ethylene, a propylene, etc.). :(CH3O)3SiCH to which it sets like 1 operative condition and this compound is expressed with the following formulas -- setting like 31 operative condition 2 Si (OCH3) 2 CH, this compound is a tetra-ethoxy silane.

[0142] For the example of a useful silane coupling agent N- (2-aminoethyl)-3-aminopropyl trimethoxysilane; 3- (N-styryl methyl-2-aminoethyl amino) propyltrimethoxysilane; -- 3-aminopropyl triethoxysilane; -- bis(2-hydroxyethyl)-3-aminopropyl-triethoxysilane; -- beta- (3 --) 4-epoxycyclohexyl ethyltrimethoxysilane; 3-glycidoxypropyltrimetoxysilane; 3-methacryloxypropyltrimethoxysilane; 3-chloropropyltrimetoxysilane; -- vinyl-trichlorosilane; -- vinyltriethoxysilane; -- vinyl-tris (2-methoxyethoxy) silane; -- aminopropyl trimethoxysilane; -- N-methylamino propyltrimethoxysilane; -- And N-phenylamino propyltrimethoxysilane is mentioned.

[0143] The :N-(3-acrylic oxy--2-hydroxypropyl)-3-aminopropyl triethoxysilane by which the following is also mentioned to a silane coupling agent again, 3-acrylic oxy-propyltrimethoxysilane, allyl compound triethoxysilane, Allyl compound trimethoxysilane, 4-amino epoxybutyltriethoxysilane, Phenethyl trimethoxysilane, N-(2-aminoethyl-3-aminopropyl) trimethoxysilane, (Aminoethyl aminomethyl) N-(2-aminoethyl-3-aminopropyl) tris (2-ethyl HEKISOKISHI) silane, 6-(amino hexylamino propyl) trimethoxysilane, aminophenyl trimethoxysilane, 3-(1-amino propoxy)-3 and 3-dimethyl-1-propenyl trimethoxysilane, 3-aminopropyl tris (methoxyethoxy ethoxy) silane, 3-aminopropyl triethoxysilane, 3-aminopropyl trimethoxysilane, omega-amino undecyl trimethoxysilane, 3-[2-N-benzylamino ethylaminopropyl] trimethoxysilane, Bis(2-hydroxyethyl)-3-aminopropyl triethoxysilane, 8-BUROMO octyl trimethoxysilane, BUROMO phenyltrimethoxysilane, 3-BUROMO propyltrimethoxysilane, p-(chloro methyl) phenyltrimethoxysilane, Chloro methyl triethoxysilane, chlorophenyl triethoxysilane, 3-chloropropyl triethoxysilane, 3-chloropropyltrimetoxysilane, 2-cyano ethyltriethoxysilane, 2-cyano ethyltrimethoxysilane, Trimethoxysilane, 3-cyano propyl triethoxysilane, (Cyano methyl phenethyl) 3-cyclopentadienyl propyl triethoxysilane, trimethoxysilane (N and N-diethyl-3-aminopropyl), Diethyl phosphato ethyltriethoxysilane, trimethoxysilane (N and N-dimethyl-3-aminopropyl), 2-(diphenyl phosphino) ethyltriethoxysilane, 2-(3, 4-epoxycyclohexyl) ethyltrimethoxysilane, 3-iodine propyltrimethoxysilane, 3-isocyanato propyl triethoxysilane, 3-mercapto propyl triethoxysilane, 3-mercapto propyltrimethoxysilane, 3-methacryloxypropyltrimethoxysilane, 3-metacryloxy propyl tris (methoxyethoxy) silane, 3-methoxy propyltrimethoxysilane, N-methylamino propyltrimethoxysilane, An N-phenethyl-N'-triethoxy silyl propyl urea, N-phenylamino propyltrimethoxysilane, 3-(N-styryl methyl-2-aminoethyl amino) propyltrimethoxysilane, 3-thio SHIANATO propyl triethoxysilane, N-(3-triethoxy silyl propyl) acetyl glycinamide, A triethoxy silyl propyl-ethyl carbamate, N-[3-(triethoxy silyl) propyl]-4, a 5-

dihydroimidazole, An N-triethoxy silyl-propyl-o-MENTO carbamate, N-[3-(triethoxy silyl) propyl] phthalamide acid (phthalamic acid), N-(triethoxy silyl propyl) urea, 1-trimethoxysilyl -2 -(p, m-chloro methyl)- Phenyl ethane, beta-trimethoxysilyl ethyl-2-pyridine, N-(3-trimethoxysilylpropyl)-N-methyl-N, and N-diaryl ammonium chloride, Trimethoxysilylpropyl diethylenetriamine, N-[(3-trimethoxy-silyl) propyl] ethylenediamine triacetic-acid 3 sodium salt, Trimethoxysilylpropyl iso CHIOURONIUMU chloride, N-(3-trimethoxysilylpropyl) pyrrole, N-trimethoxysilylpropyl tree N-butyl ammonium bromide and N-trimethoxysilylpropyl - N, N, and N-trimethylammonium chloride. Vinyltriethoxysilane, a vinyl triisopropoxy silane, vinyltrimetoxysilane, vinyl tris-t-butoxysilane, a vinyl tris (2-methoxyethoxy) silane, vinyl TORIISO propenoxysilane, and a vinyl tris (t-butylperoxy) silane are also mentioned to a silane coupling agent again.

[0144] The :2-acetoxy ethyl trichlorosilane by which the following is further mentioned to a silane coupling agent, 3-acrylic oxy-propyl trichlorosilane, allyltrichlorosilane, 8-BUROMO octyl trichlorosilane, BUROMO phenyl trichlorosilane, 3-BUROMO propyl trichlorosilane, 2-(KARUBO methoxy) ethyl trichlorosilane, 1-chloro ethyl trichlorosilane, 2-chloro ethyl trichlorosilane, p-(chloro methyl) phenyl trichlorosilane, chloro methyltrichlorosilane, Chlorophenyl trichlorosilane, 3-chloropropyl trichlorosilane, Trichlorosilane, 2-cyano ethyl trichlorosilane, (3-cyano butyl) 3-cyano propyl trichlorosilane, trichlorosilane (dichloro methyl), Trichlorosilane, 6-HEKISHI-1-enyl trichlorosilane, (Dichlorophenyl) 3-methacrylic-oxy-propyl trichlorosilane, 3-(4-methoxypheny) propyl trichlorosilane, 7-oct-1-enyl trichlorosilane, 3-(N-phthalimide) propyl trichlorosilane, 1-trichlorosilyl-2-(p, m-chloro methylphenyl) ethane, 4-[2-(trichlorosilyl) ethyl] cyclohexene, 2-[2-(trichlorosilyl) ethyl] pyridine, 4-[2-(trichlorosilyl) ethyl] pyridine, 3-(trichlorosilyl) propyl chloro formate, and vinyl trichlorosilane.

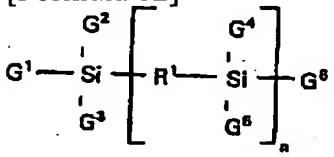
[0145] Aminopropyl trimethoxysilane, a tetra-ethoxy silane, bis(2-hydroxyethyl)-3-aminopropyl triethoxysilane, 3-(N-styryl methyl-2-aminoethyl amine) propyltrimethoxysilane, 3-glycidoxypropyltrimetoxysilane, N-methylamino propyltrimethoxysilane, 2-(2-aminoethyl-3-aminopropyl) trimethoxysilane, and N-phenylamino propyltrimethoxysilane are especially mentioned to a useful silane coupling agent.

[0146] Setting like 1 operative condition, a silane coupling agent is except 3-glycidoxypropyltrimetoxysilane.

[0147] In another embodiment, silanizing includes deposition of two or more silane compounds. As expressed below, one of two or more silanes is a silane (A) typically, and others are silanes (B).

[0148] A silane (A) is : [0149] which is the compound expressed with the following formulas.

[Formula 12]

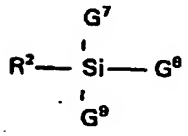


[0150] G1, G2, G3, and G4, G5 and G6 are a halogen, a hydrocarbyloxy radical, or a hydroxy group independently,;R1 is a hydrocarbon group or a nitrogen content hydrocarbon group here, and; and n are 0 or 1. It sets like 1 operative condition, and chloro and alkoxy ** alkoxy alkoxy **** are with alkoxy alkoxy alkoxy **, and G1, G2, G3, and each of G4, G5, and G6 of R1 are monoamino -, poly amino-permutation alkylene groups, or arene radicals to the alkylene group of the carbon atom to about ten pieces, an arene radical, or about ten carbon atoms independently. It sets like 1 operative condition, and G1, G2, G3, and each of G6 are the alkoxy groups, the alkyl alkoxy groups, alkoxy alkoxy groups, or alkoxy alkoxy alkoxy groups of a carbon atom to about ten pieces, and n is 0.

[0151] :tetramethoxy silane to which the following is mentioned as an example of a silane (A), A tetra-ethoxy silane, tetra-propoxysilane, tetra--n-butoxysilane, A tetrakis (2-ethoxy ethoxy) silane, a tetrakis (2-ethyl butoxy) silane, A tetrakis (2-ethyl HEKISOKISHI) silane, a tetrakis (methoxyethoxy ethoxy) silane, A tetrakis (2-methoxyethoxy) silane, a tetrakis (1-methoxy-2-propoxy) silane, A bis[3-(triethoxy silyl) propyl] amine, bis[3-(trimethoxysilyl) propyl] ethylenediamine, 1, 2-bis(trimethoxysilyl) ethane, bis(trimethoxysilyl ethyl) benzene, 1, a 6-bis(trimethoxysilyl) hexane, 1, 2-bis(trichlorosilyl) ethane, 1, a 6-bis(trichlorosilyl) hexane and 1, a 8-bis(trichlorosilyl) octane.

[0152] A silane (B) is a compound expressed with the following formulas, and is : [0153].

[Formula 13]



[0154] R2 is an organic functional group and this organic functional group is said another substrate and reactivity here, or it has the compatibility over this and;, and G7, G8 and G9 are a halogen, hydrocarbyloxy, or a hydroxy group independently. Setting like 1 operative condition, R2 is amino -, hydroxy -, and/or an alkoxy-content hydrocarbon group. Setting like 1 operative condition, each of G7, G8, and G9 is chloro, methoxy, or ethoxy ******.

[0155] For the example of a silane (B) N- (2-aminoethyl)-3-aminopropyl trimethoxysilane; 3- (N-styryl methyl-2-aminoethyl amino) propyltrimethoxysilane; -- 3-aminopropyl triethoxysilane; -- bis(2-hydroxyethyl)-3-aminopropyl-triethoxysilane; -- beta- (3 --) 4-epoxycyclohexyl ethyltrimethoxysilane; 3-glycidoxypropyltrimetoxysilane; 3-methacryloxypropyltrimethoxysilane; 3-chloropropyltrimetoxysilane; -- vinyl-trichlorosilane; -- vinyltriethoxysilane; -- vinyl-tris (2-methoxyethoxy) silane; -- aminopropyl trimethoxysilane; -- N-methylamino propyltrimethoxysilane; -- And N-phenylamino propyltrimethoxysilane is mentioned.

[0156] The :N-(3-acrylic oxy--2-hydroxypropyl)-3-aminopropyl triethoxysilane by which the following is also mentioned as the example of a silane (B) again, 3-acrylic oxy-propyltrimethoxysilane, allyl compound triethoxysilane, Allyl compound trimethoxysilane, 4-amino epoxybutyltriethoxysilane, Phenethyl trimethoxysilane, N-(2-aminoethyl-3-aminopropyl) trimethoxysilane, (Aminoethyl aminomethyl) N-(2-aminoethyl-3-aminopropyl) tris (2-ethyl HEKISOKISHI) silane, 6-(amino hexylamino propyl) trimethoxysilane, aminophenyl trimethoxysilane, 3-(1-amino propoxy)-3 and 3-dimethyl-1-propenyl trimethoxysilane, 3-aminopropyl tris (methoxyethoxy ethoxy) silane, 3-aminopropyl triethoxysilane, 3-aminopropyl trimethoxysilane, omega-amino undecyl trimethoxysilane, 3-[2-N-benzylamino ethylaminopropyl] trimethoxysilane, Bis(2-hydroxyethyl)-3-aminopropyl triethoxysilane, 8-BUROMO octyl trimethoxysilane, BUROMO phenyltrimethoxysilane, 3-BUROMO propyltrimethoxysilane, p-(chloro methyl) phenyltrimethoxysilane, Chloro methyl triethoxysilane, chlorophenyl triethoxysilane, 3-chloropropyl triethoxysilane, 3-chloropropyltrimetoxysilane, 2-cyano ethyltriethoxysilane, 2-cyano ethyltrimethoxysilane, Trimethoxysilane, 3-cyano propyl triethoxysilane, (Cyano methyl phenethyl) 3-cyclopentadienyl propyl triethoxysilane, trimethoxysilane (N and N-diethyl-3-aminopropyl), Diethyl phosphato ethyltriethoxysilane, trimethoxysilane (N and N-dimethyl-3-aminopropyl), 2-(diphenyl phosphino) ethyltriethoxysilane, 2-(3, 4-epoxycyclohexyl) ethyltrimethoxysilane, 3-iodine propyltrimethoxysilane, 3-isocyanato propyl triethoxysilane, 3-mercapto propyl triethoxysilane, 3-mercapto propyltrimethoxysilane, 3-methacryloxypropyltrimethoxysilane, 3-metacryloxy propyl tris (methoxyethoxy) silane, 3-methoxy propyltrimethoxysilane, N-methylamino propyltrimethoxysilane, An N-phenethyl-N'-triethoxy silyl propyl urea, N-phenylamino propyltrimethoxysilane, 3-(N-styryl methyl-2-aminoethyl amino) propyltrimethoxysilane, 3-thio SHIANATO propyl triethoxysilane, N-(3-triethoxy silyl propyl) acetyl glycinamide, A triethoxy silyl propylethyl carbamate, N-[3-(triethoxy silyl) propyl]-4, a 5-dihydroimidazole, An N-triethoxy silyl-propyl-o-MENTO carbamate, N-[3-(triethoxy silyl) propyl] phthalamide acid, N-(triethoxy silyl propyl) urea, 1-trimethoxysilyl -2 -(p, m-chloro methyl)- Phenyl ethane, beta-trimethoxysilyl ethyl-2-pyridine, N(3-trimethoxysilylpropyl)-N-methyl-N, and N-diaryl ammonium chloride, Trimethoxysilylpropyl diethylenetriamine, N-[(3-trimethoxysilyl) propyl] ethylenediamine triacetic-acid 3 sodium salt, Trimethoxysilylpropyl iso CHIOURONIUMU chloride, N-(3-trimethoxysilylpropyl) pyrrole, N-trimethoxysilylpropyl tree N-butyl ammonium bromide and N-trimethoxysilylpropyl - N, N, and N-trimethylammonium chloride. Vinyltriethoxysilane, a vinyl triisopropoxy silane, vinyltrimetoxysilane, vinyl tris-t-butoxysilane, a vinyl tris (2-methoxyethoxy) silane, vinyl TORIISO propenoxysilane, and a vinyl tris (t-butylperoxy) silane are also mentioned as the example of a silane (B) again.

[0157] The :2-acetoxy ethyl trichlorosilane by which the following is further mentioned as the example of a silane (B), 3-acrylic oxy-propyl trichlorosilane, allyltrichlorosilane, 8-BUROMO octyl trichlorosilane, BUROMO phenyl trichlorosilane, 3-BUROMO propyl trichlorosilane, 2-(KARUBO methoxy) ethyl trichlorosilane, 1-chloro ethyl trichlorosilane, 2-chloro ethyl trichlorosilane, p-(chloro methyl) phenyl trichlorosilane, chloro methyltrichlorosilane, Chlorophenyl trichlorosilane, 3-chloropropyl trichlorosilane, Trichlorosilane, 2-cyano ethyl trichlorosilane, (3-cyano butyl) 3-cyano propyl trichlorosilane, trichlorosilane (dichloro methyl), Trichlorosilane, 6-HEKISHI-1-enyl trichlorosilane, (Dichlorophenyl) 3-metacryloxy

propyl trichlorosilane, 3-(4-methoxypheny) propyl trichlorosilane, 7-oct-1-enyl trichlorosilane, 3-(N-phthalimide) propyl trichlorosilane, 1-trichlorosilyl-2-(p, m-chloro methylphenyl) ethane, 4-[2-(trichlorosilyl) ethyl] cyclohexane, 2-[2-(trichlorosilyl) ethyl] pyridine, 4-[2-(trichlorosilyl) ethyl] pyridine, 3-(trichlorosilyl) propyl chloro formate, and vinyl trichlorosilane.

[0158] It sets like 1 operative condition, and the weight ratio of a silane (A) and a silane (B) has about 5:95 - a desirable abbreviation 95:5, and about 10:90 - its abbreviation 90:10 are still more desirable.

[0159] It sets like 1 operative condition and two silane surface treatment is guided combining a tetra-ethoxy silane or a tetramethoxy silane from the constituent containing N-(2-aminoethyl-3-aminopropyl) trimethoxysilane, 3-aminopropyl trimethoxysilane, or 3-glycidoxypropyltrimetoxysilane.

[0160] Do application to the copper foil of two silane surface treatment by applying a silane (A) and the neat mixture of (B) to a foil front face. However, generally it is desirable to mix a silane in the medium which was suitable before applying them to a foil front face. A silane or silanes are either of whether it may be separately mixed with whether it may be mixed with a medium at one process,;, or a medium, and before spreading on a foil front face, it combines the mixture subsequently obtained. Or a separate solution can be continuously applied to copper, and between spreading, it dries or does not dry. Silane mixture may be applied to a foil front face with the gestalt of the aqueous emulsion of the mixture of a water dispersion or a water solution, water, and alcohol, a suitable organic solvent, the water emulsion of silane mixture, or the solution of the silane mixture in a suitable organic solvent. The conventional organic solvent may be used. These contain alcohol, the ether, a ketone and aliphatic hydrocarbon, aromatic hydrocarbon, or the mixture of the amide and these like N.N-dimethylformamide. A useful solvent is a solvent which has good humidity and drying characteristics, for example, contains water, ethanol, isopropanol, and a methyl ethyl ketone. The aqueous emulsion of a silane or silane mixture may be formed by the conventional approach which used the conventional dispersant and conventional surfactant containing a nonionic dispersant. Although there may be a silane in such a solution or an emulsion or concentration of silane mixture to about 100% of the weight of such a silane, it is about 0.1 % of the weight - about 5% of the weight of the range preferably. One or two silane surface preparation may be applied to a foil front face using the well-known applying method containing reverse roller coating (reverse roller coating), doctor blade coating (doctor blade coating), immersion, paint, and a spray.

[0161] Application of one or two silane surface treatment on the front face of a foil is typically performed at the temperature of about 15 degrees C - about 45 degrees C, and it is about 20 degrees C - about 30 degrees C preferably. Following application of the silane surface treatment on the front face of a foil, a foil may be heated for abbreviation 0.03- about 5 minutes, in order to raise surface desiccation preferably to the temperature of about 60 degrees C - about 170 degrees C. The thickness of the desiccation film of the silane surface treatment on a foil is about 0.002 - 0.1 microns of abbreviation preferably, and is about 0.005 - 0.02 microns of abbreviation still more preferably.

[0162] (Example 13) Two flexible layered products are offered, one is the same as before and one follows this invention. The 1st flexible layered product (former) is the same as the 1st flexible layered product indicated by the example 1. the 2nd flexible layered product (this invention is followed) -- oxidation treatment -- in addition, except for contacting the water solution which contains about 2% of the weight of 3-aminopropyl triethoxysilane in 25 degrees C, and subsequently heating one side of a copper layer at 100 degrees C for 5 minutes, it is the same as the 2nd flexible layered product of an example 4.

[0163] A bending cycle similar to what was shown in drawing 1 is presented with a flexible layered product. At intervals of 5,000,000 cycles, copper foil is examined by one about 1600 times the dilation ratio of this, and existence of a minute crack and extent are determined. The 1st flexible layered product shows the minute crack of some [5,000,000 cycle], and the minute crack (minding copper foil partly) which spread in 10,000,000 cycles. The 2nd flexible layered product shows the minute crack of some [20,000,000 cycle], and the minute crack (minding copper foil partly) which spread in 30,000,000 cycles.

[0164] (Example 14) Two flexible layered products are offered, one is the same as before and one follows this invention. The 1st flexible layered product (former) is the same as the 1st flexible layered product indicated by the example 1. the 2nd flexible layered product (this invention is followed) -- oxidation treatment -- in addition, if it removes contacting the water solution which contains about 0.75% of the weight of N-(2-aminoethyl-3-aminopropyl) trimethoxysilane, and about 0.75% of the weight of a tetramethoxy silane in 25 degrees C, and heating one side of a copper layer at 100 degrees C for 5 minutes subsequently, it is the same as the 2nd flexible layered product of an example 4.

[0165] A bending cycle similar to what was shown in drawing 1 is presented with a flexible layered product. At intervals of 5,000,000 cycles, copper foil is examined by one about 1600 times the dilation ratio of this,

and existence of a minute crack and extent are determined. The 1st flexible layered product shows the minute crack of some [5,000,000 cycle], and the minute crack (minding copper foil partly) which spread in 10,000,000 cycles. The 2nd flexible layered product shows the minute crack of some [25,000,000 cycle], and the minute crack (minding copper foil partly) which spread in 35,000,000 cycles.

[0166] In some embodiments, in order [one] to prevent a minute crack, it is desirable to use many copper foil processings. for example, one operative condition -- like -- setting -- copper foil -- the inside of an acid copper-sulfate tub -- it cathode-processes, and silanizing is presented continuously. another operative condition -- like -- setting -- copper foil -- zinc deposition processing -- continuing -- again -- the inside of a chromate tub -- it cathode-processes, and silanizing is presented continuously. in addition, another operative condition -- the inside of the acid tank with which it sets like and copper foil contains zinc ion, chromate ion, and a hydrogen inhibitor -- it cathode-processes, and silanizing is presented continuously. further in addition another operative condition -- the inside of the acid tank containing the oxidation, the zinc ion, the underwater chromate ion, and underwater hydrogen inhibitor which sets like and carries out aeration of the copper foil -- it cathode-processes, and silanizing is presented continuously. It sets in the another embodiment and spreading of the tie coat layer which brown-oxidizes, or black-oxidizes, and uses chromium as the base continuously is presented with copper foil. Generally, it is desirable to combine metal base processing or oxidation treatment with silanizing.

[0167] The flexible circuit of this invention is at least one which is a flexible polymer film, and contains two polymer substrates typically. Although a flexible polymer substrate contains at least one thermosetting resin and thermoplastics, it contains at least one polyester resin, polyimide resin, and a condensation polymer typically. a flexible substrate -- the thickness of the range to about 0.2mm -- having -- one operative condition -- like -- setting -- the thickness of about 5 micrometers - about 0.15mm -- having -- another operative condition -- like -- setting -- the thickness of about 10 micrometers - about 5000 micrometers -- having -- still more nearly another operative condition -- it sets like and has the thickness of about 15 micrometers - about 1000 micrometers. With a filter, UBUN (woven) glass, non-UBUN glass, and/or other fibrous ingredients, there is a flexible substrate, it is, and may be formed in the talk. A flexible substrate may be a monolayer-ized film or a multilayering film.

[0168] In the thermosetting resin which may be used in order to form a flexible substrate Phenol resin, phenolplast, furan resin, amino-PURASUTO (plast) resin, Alkyd resin, allylic resin, an epoxy resin, an epoxy PUREPU leg, Polyurethane resin, thermosetting polyester resin, polyimide screw-maleimide resin, A polymaleimide-epoxy resin, polymaleimide-isocyanate resin, Silicone resin, cyanate resin, a cyanate-epoxy resin, cyanate-polymer RAID resin, cyanate-epoxy-polymaleimide resin, bismaleimide triazine resin, etc. are mentioned.

[0169] In thermoplastics, the Pori alpha olefin, polyethylene, polypropylene, The Pori 4-methyl-pentene -1, ethylene / vinyl copolymer, an ethylene vinyl acetate copolymer, An ethylene acrylic-acid copolymer, an ethylene methacrylate copolymer, Ethylene methyl acrylate copolymer etc.; Polypropylene, thermoplastic propylene polymers [, such as an ethylene-propylene copolymer,]; -- vinyl chloride polymer and copolymer; -- vinylidene chloride polymer and copolymer; -- polyvinyl alcohol; -- an acrylic acid -- The acrylic polymer; polyester; polyimide; condensation polymer which consists of a methacrylic acid, methyl acrylate, methacrylate, acrylamide, etc.; Polytetrafluoroethylene, Poly vinylidene fluoride and fluorocarbon resin like fluorinated-ethylene-propylene resin; styrene resin, such as polystyrene, alpha methyl styrene, high impact polystyrene, and an acrylonitrile butadiene-styrene polymer, is mentioned.

[0170] Polyester resin contains the resin generated from dibasicity aliphatic series, aromatic carboxylic acid and diol, or triol. These contain polyethylene terephthalate, polyethylenenaphthalate, polybutylene terephthalate (teraphthlate), etc. The polycarbonate which is long-chain straight chain polyester guided from carbonic acid (for example, phosgene) and a dihydric phenol (for example, bisphenol A) may be used.

[0171] Especially polyimide resin is useful in a flexible substrate. These may be generated by the reaction including the process at which tetrabasic acid 2 anhydride and the aromatic series diamine which gives a polyamide acid to the beginning and is converted by heat or the catalyst subsequently to the amount straight chain polyimide of giant molecules are contacted.

[0172] A useful condensation polymer contains a polyamide, polyether imide, polysulfone, polyether sulphone, polybenzazole, aromatic series polysulfone, polyphenylene oxide, a polyether ether ketone, etc.

[0173] The desirable ingredients in a flexible substrate are polyethylene terephthalate, polybutylene terephthalate, and a polyester film ingredient like polyimide. These film materials are DuPont. Allied-Apical Teijin Kanega-fuchi and Ube It is sold by Industries by various trade names containing Mylar (trademark), Kapton (trademark), Apical (trademark), and Upilex (trademark).

[0174] Even if it processes before adding a copper layer there, it is not necessary to carry out a flexible substrate. For example, an adhesion promoter like adhesives may be applied to a flexible substrate in order to raise adhesion to a copper layer. The example of the adhesives which may be used contains the adhesives which used as the base the adhesives which used epoxy as the base, the adhesives which used polyimide as the base, and an acrylic. These are independent or can be used combining a phenol or polyvinyl butyral resin. adhesives -- the thickness of the range to about 0.1mm -- having -- one operative condition -- like -- setting -- the thickness of about 5 micrometers - about 5000 micrometers -- having -- another operative condition -- like -- setting -- the thickness of about 10 micrometers - about 1000 micrometers -- having -- still more nearly another operative condition -- it sets like and has the thickness of about 15 micrometers - about 500 micrometers.
[0175] or [carrying out the laminating of the copper layer to processing or an unsettled flexible substrate] -- or it is made to deposit or [that an adhesion promoter may exist between copper foil and a flexible substrate] -- or it cannot exist. The deposited copper layer may be front-formed in copper foil, or may be formed using various well-known techniques, and this technique includes electroplating, non-electroplating and vacuum evaporationo, or those combination. a copper layer -- the thickness to about 70 micrometers -- having -- one operative condition -- like -- setting -- the thickness of about 2 micrometers - about 60 micrometers -- having -- another operative condition -- it sets like and has the thickness of about 5 micrometers - about 40 micrometers. It sets like 1 operative condition, this copper layer has the thickness of about 5 micrometers, and it sets like 1 operative condition, has the thickness of about 10 micrometers, it sets like 1 operative condition, has the thickness of about 15 micrometers, it sets like 1 operative condition, has the thickness of about 18 micrometers, it sets like 1 operative condition, and has the thickness of about 35 micrometers.
[0176] Electroplating includes electric deposition of metal coating to the electrode surface top for forming a metal deposit. The electrode surface processed is used as the cathode in an electroplating solution or an electroplating bath. Such a tub is a typical water solution and a metal is returned by the flow of a current through the solution of a metal salt from there. In case metaled electroplating is performed on a conductive electrode, an electrode and a substrate are often immersed in washing, a rinse, and an acid, or other pretreatments or preparation of a substrate is presented with them. When operating an electroplating process, it is immersed into a solution and, as for a substrate, a metal anode to a substrate cathode passes a typically required current. A solution is often agitated and is minutely controlled using the principle of common knowledge of temperature, a current, metal concentration, and other variables.
[0177] A copper layer may be formed again using non-electroplating, and this is the autocatalysis nature deposition by which the film which continued by the interaction between a metal and a chemistry reducing agent in the solution of a metal salt was controlled. Non-electrical-and-electric-equipment deposition can give a metal, an alloy, metallic compounds, and the film of composite material on conductivity and a non-conductive front face. A non-conductive solution contains a metal salt, a reducing agent, pH regulator or a buffer, a compound agent, and one or more additives, in order to control solution stability, a film property, the rate of sedimentation, etc. The advantage of non-electroplating is being able to galvanize a metal on non-conductive or a ******** front face. Since the copper which has the thickness to about 70 micrometers is deposited again so that it may be described above, both a vacuum evaporationo technique, and PVD and CVD may be used.
[0178] When a copper layer is applied to one flexible substrate, a flexible print wire board (printed wiring board) may once be produced by forming a circuit pattern. A circuit pattern can be formed using a photograph monotonous technique including an etching process, and it is used here in order to remove alternatively the copper from which the circuit pattern of the copper foil patternized in the resistance tub and the etching fluid tub is separated. An adhesion promoter is applied to the side which copper foil exposed if needed, and another processing or an unsettled flexible substrate is fixed to the copper foil covering layered product patternized in order to form a flexible circuit.
[0179] Various processings of this invention may be performed with a continuous magnetization method using a single chamber, and this chamber is divided into the partition operated by the pressure optimized by each processing. Various processings may be performed with a continuous magnetization method in each processing again using a separate chamber. Various treatment may be performed again with the gradual continuous magnetization method which uses two or more passage which passes along a single chamber and a chamber, in order to offer each process stroke.
[0180] Although this invention is explained in relation to the desirable embodiment, the various alterations are clear for this contractor, if a specification is read. Therefore, it should be understood that it is meant that

this invention indicated in this specification includes such an alteration that is within the limits of an attached application for patent.

[0181] It is the copper layer which has a minute crack prevention layer in one side at least. one operative condition -- like -- setting -- this invention -- flexible polymer film [of ** a first]; -- In the copper layer in which a minute crack prevention layer has the thickness to about 18 micrometers of a flexible layered product Between the bending cycles of at least 50,000,000, And/or, it is related with the flexible layered product containing sufficient copper layer; to prevent a minute crack between the bending cycles of at least 20,000,000 in the copper layer which has the thickness to about 35 micrometers, and the second flexible polymer film.

[0182]

[Effect of the Invention] The flexible circuit which has improved electrical characteristics is offered as a result of this invention. The flexible circuit which has improved electrical characteristics shows the improved resistance over mechanical fatigue, therefore shows the improved resistance over damage on a copper foil coat, and, thereby, improves electrical characteristics. The improved resistance over mechanical fatigue can cause [tolerant] enhancement over the minute crack of a copper foil coat.

[0183] Moreover, the flexible circuit which has bending improved in order to introduce a property is also offered as a result of this invention. In this relation, this invention offers the flexible circuit which has the resistance over both a high cycle, low distortion fatigue and a low cycle, and high distortion fatigue.

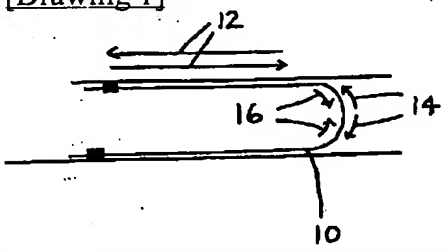
[Translation done.]

* NOTICES *

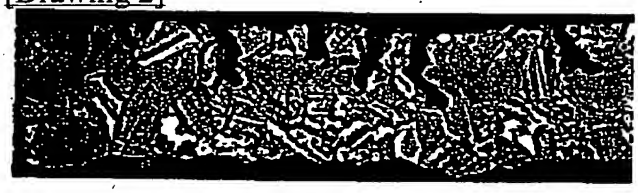
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

[Drawing 1]



[Drawing 2]



A

B

[Translation done.]